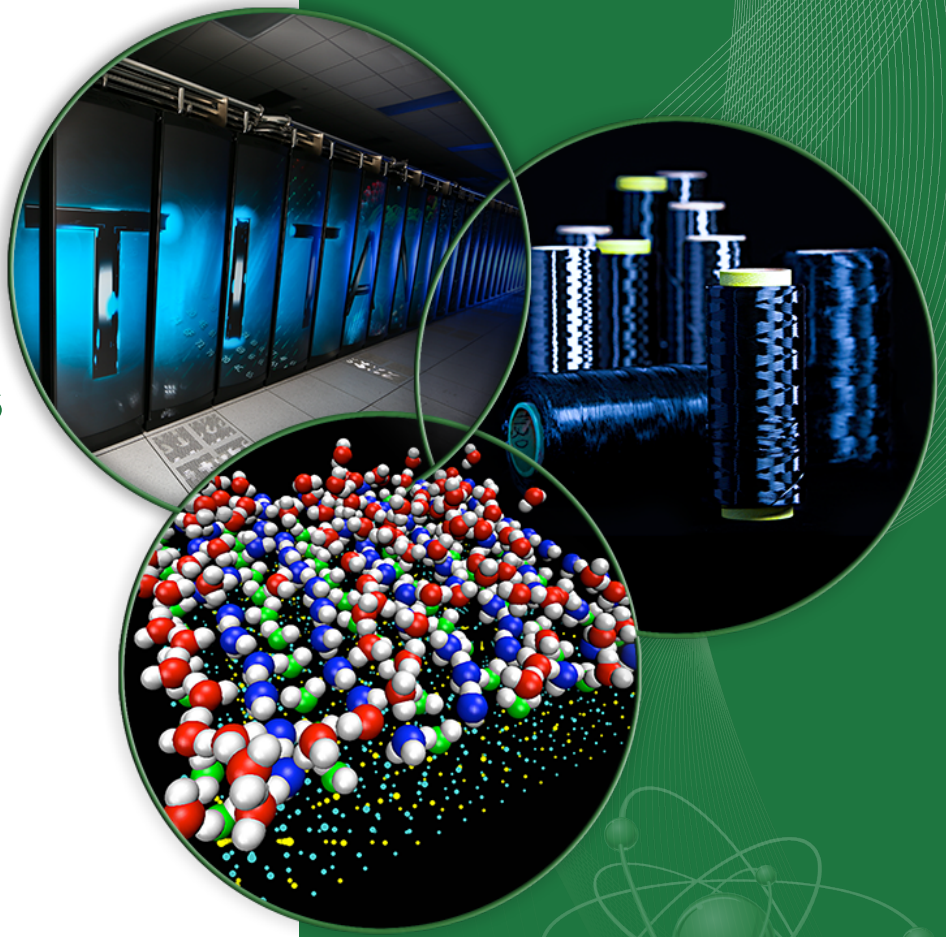
Introduction to Mössbauer spectroscopy

NRS Workshop 2017

CONUSS and Sychrotron Mössbauer Data Analysis



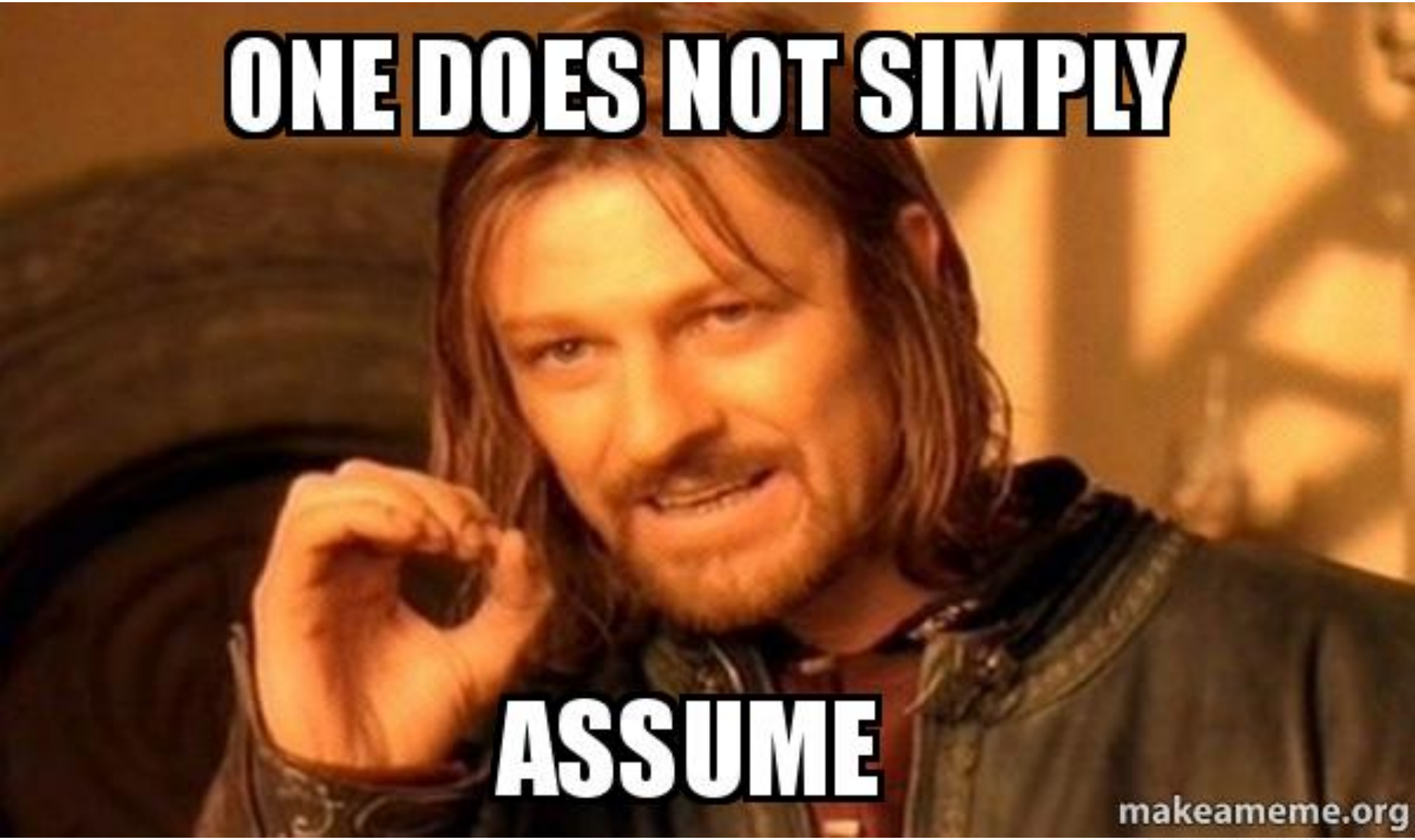
Raphaël P. Hermann

Advanced Photon Source
Argonne National Laboratory
November 16th -19th 2017

ORNL is managed by UT-Battelle
for the US Department of Energy

OAK RIDGE National Laboratory

Rule 1: Know your audience



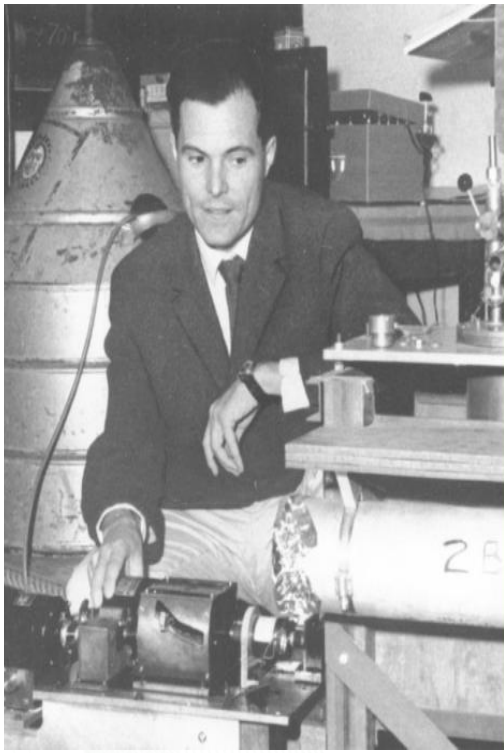
- Historical perspective
- Spectral description and parameters
- Static interactions
- Time dependent interactions

Rudolf Mößbauer (1929-2011)

Kernresonanzfluoreszenz von Gammastrahlung in ^{191}Ir

Zeitschrift für Physik, 151, pp 124-143 (1958).

Nobel Prize in Physics, 1961.

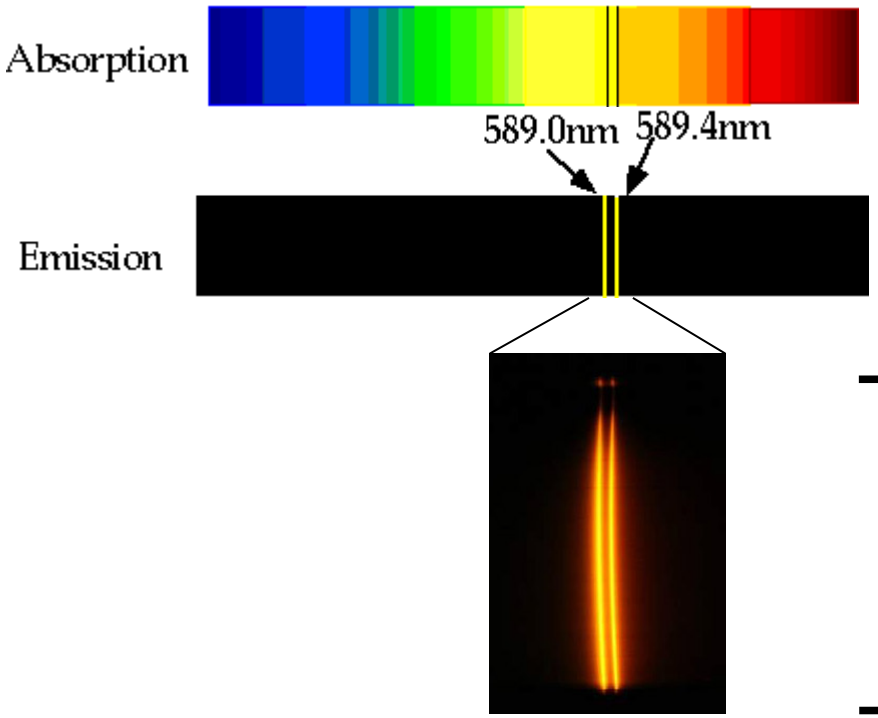


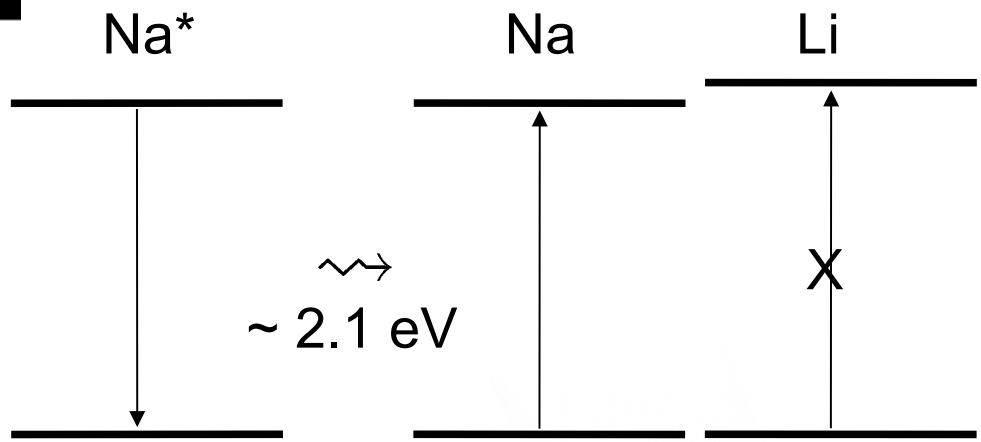
„... young people are more often apt to attack problems with unconventional approaches, which would not be touched by older, more experienced and more knowledgeable persons.“

The Rudolf Mössbauer Story,
His Scientific Work and Its Impact on Science and History,
Kalvius, Michael, Kienle, Paul (Eds.) 2012, Springer Verlag

OAK RIDGE National Laboratory

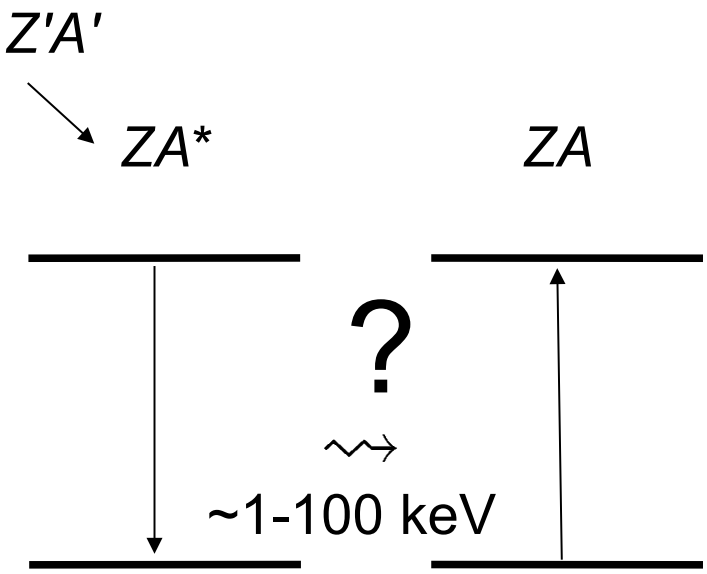
Electron transitions and resonant absorption





http://people.physics.carleton.ca/~watson/Physics/PHYS2903/2903_Quantum_Physics/PHYS2903_Bohr.html?id=0

Nuclear resonant absorption?



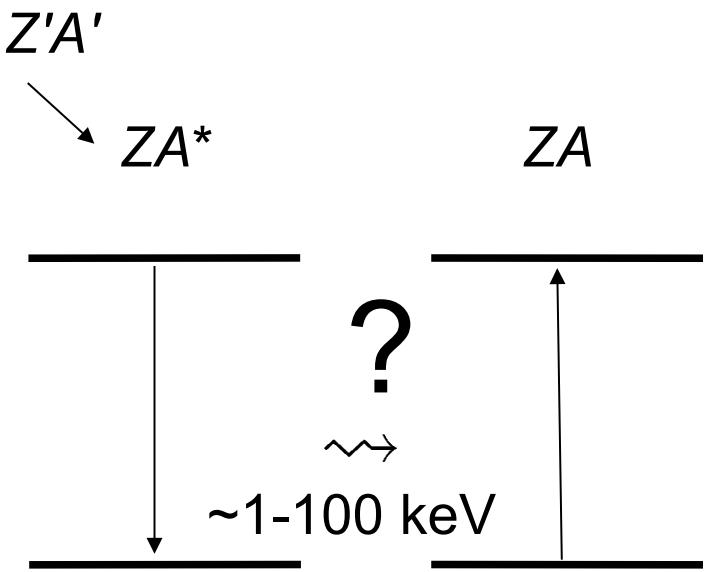
„As early as 1929, Kuhn had expressed the opinion that the **resonance absorption of gamma rays** should constitute the nuclear physics analogue to this optical resonance fluorescence. Here, a radioactive source should replace the optical light source. The gamma rays emitted by this source should be able to initiate the inverse process of **nuclear resonance absorption** in an absorber composed of nuclei of the same type as those decaying in the source.

Again, the scheme (...) would hold here, but the radiative transitions would now take place between nuclear states.

Nevertheless, **all attempts in the next two decades** to find this nuclear resonance absorption **proved fruitless**. …. it is appropriate to consider the reasons why the discovery of nuclear resonance absorption was so long delayed.

R.L. Mössbauer, Nobel Lecture, The Nobel Foundation 1961
W. Kuhn, Phil. Mag. 8, 625 (1929)

Nuclear resonant absorption?



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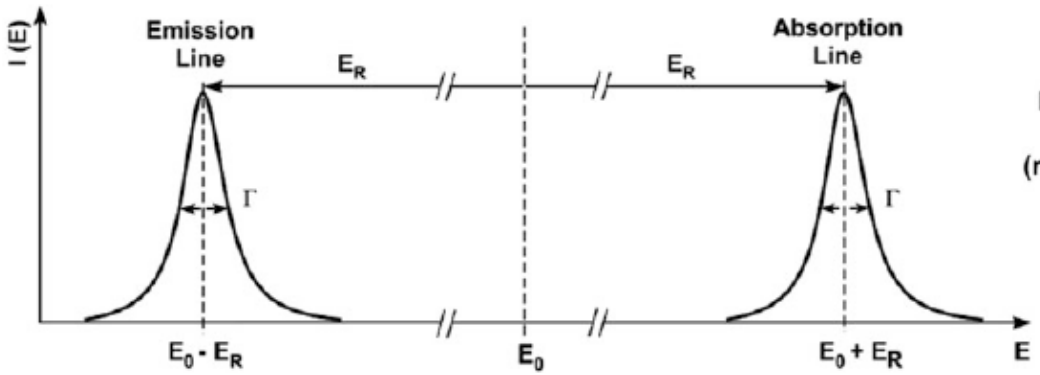
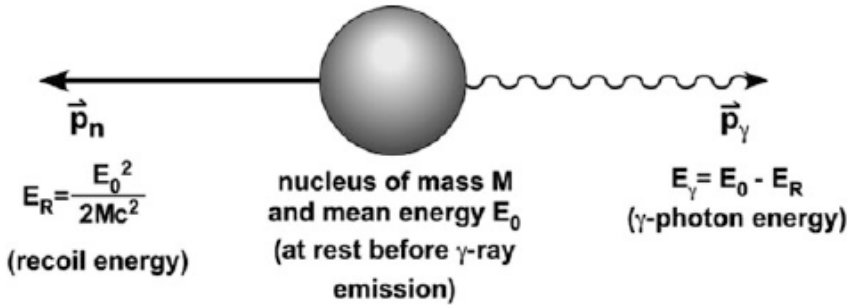
1) Conservation of momentum. Recoil energy:

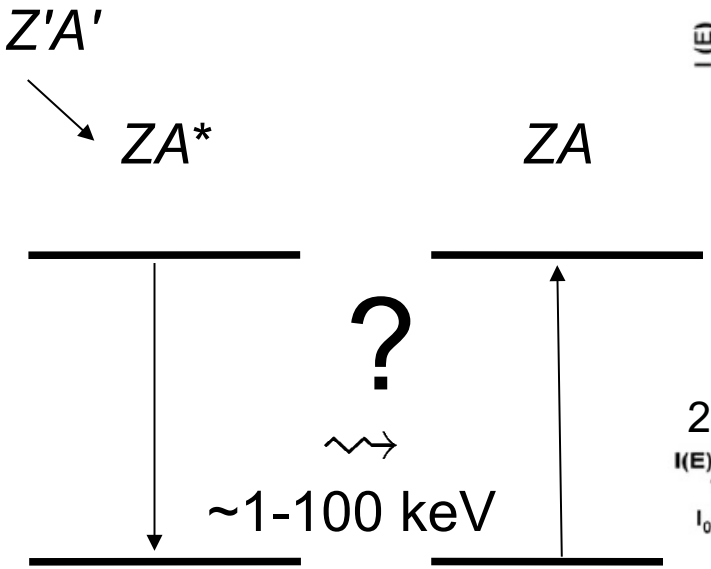




$$E_R = \frac{E_\gamma^2}{2Mc^2}$$

Gütlich, Bill, Trautwein (eds.), Mössbauer spectroscopy and Transition Metal Chemistry, Springer, 2011.

Nuclear resonant absorption?



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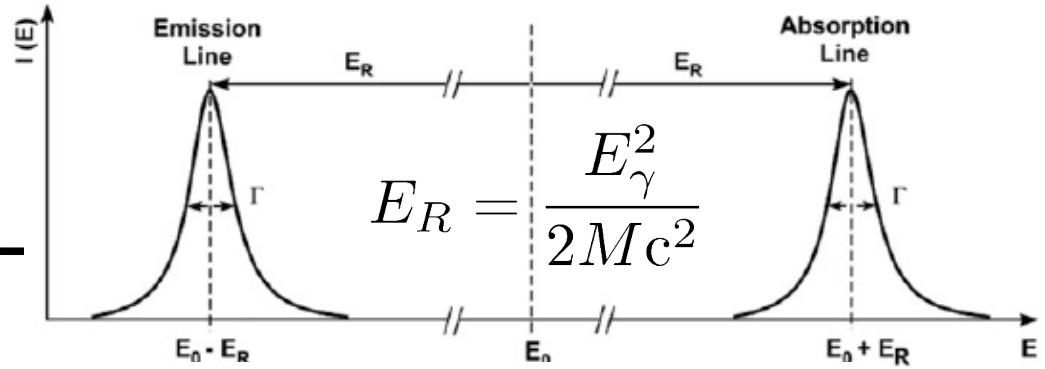
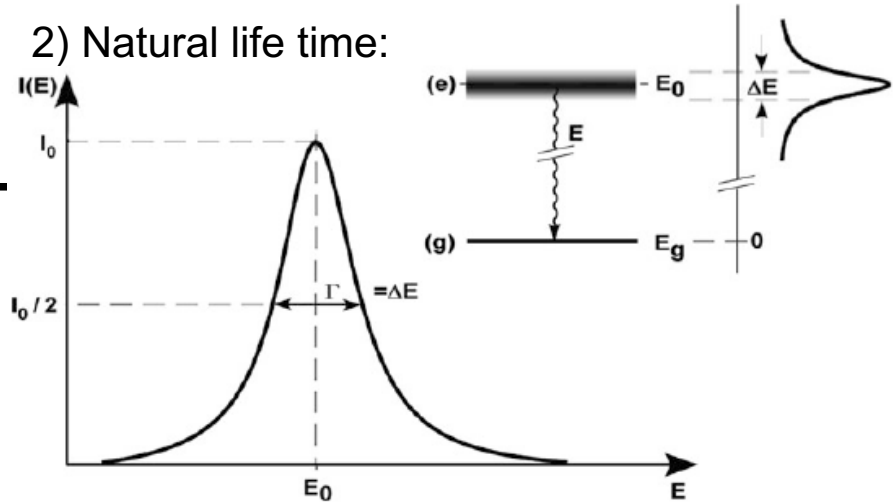


$$E_R = \frac{E_\gamma^2}{2Mc^2}$$

2) Natural life time:

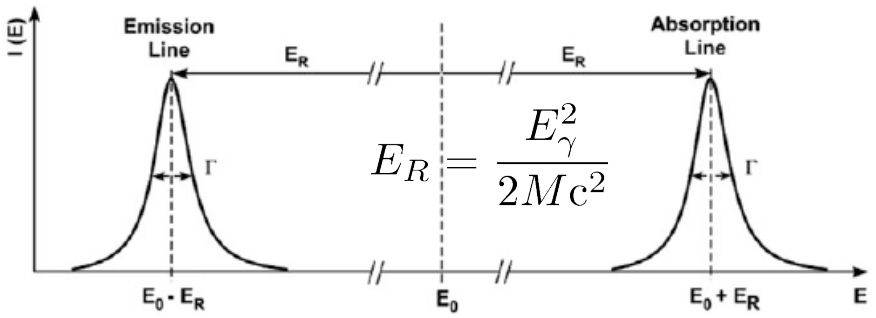


	Energy(eV)	Γ_n (eV)	E_R (eV)	$\Gamma_n/2E_R$
^{57}Fe	14400	5.10^{-9}	2.10^{-3}	**$1,2.10^{-6}$**
Na (D-line)	2.1	4.10^{-8}	1.10^{-10}	**220**

Gütlich, Bill, Trautwein (eds.), Mössbauer spectroscopy and Transition Metal Chemistry, Springer, 2011.

Nuclear resonant absorption?

1) Conservation of momentum. Recoil energy:



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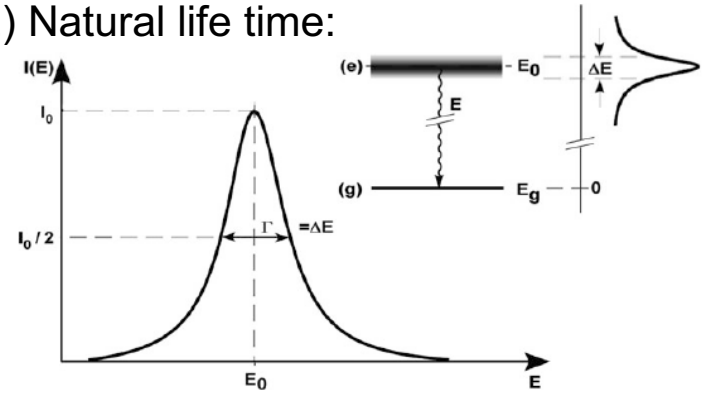


„The unsatisfactory situation with respect to nuclear resonance absorption first changed in 1951, when Moon succeeded in demonstrating the effect for the first time, by an ingenious experiment. The fundamental idea of his experiment was that of compensating for the recoil-energy losses of the gamma quanta: the radioactive source used in the experiment was moved at a suitably high velocity toward the absorber or scatterer. The displacement of the emission line toward higher energies achieved in this way through the **Doppler effect** produced a measurable nuclear fluorescence effect.“

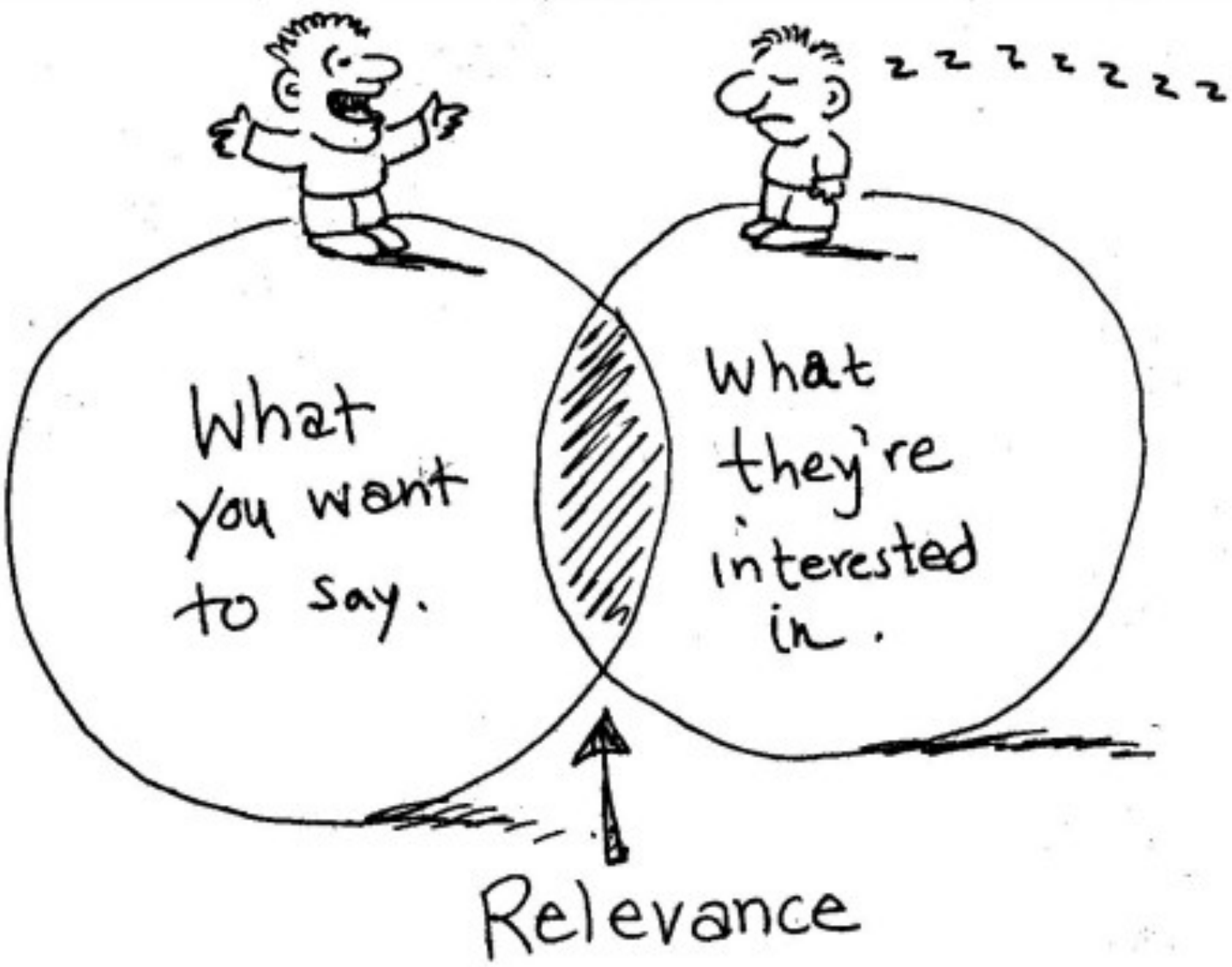
R.L. Mössbauer, Nobel Lecture, The Nobel Foundation 1961
P.B. Moon, Proc. Phys. Soc. (London) 64, 76 (1951)

„A method first employed by Malmfors appeared to be especially suitable … . In this method, a broadening of the emission or absorption line, leading to a corresponding increase in the degree of overlap of the two lines, is achieved by **increasing the temperature.**”

K.G. Malmfors, Arkiv Fysik 6, 49 (1953)

Gütlich, Bill, Trautwein (eds.), Mössbauer spectroscopy and Transition Metal Chemistry, Springer, 2011.

Rule 1: Know your audience

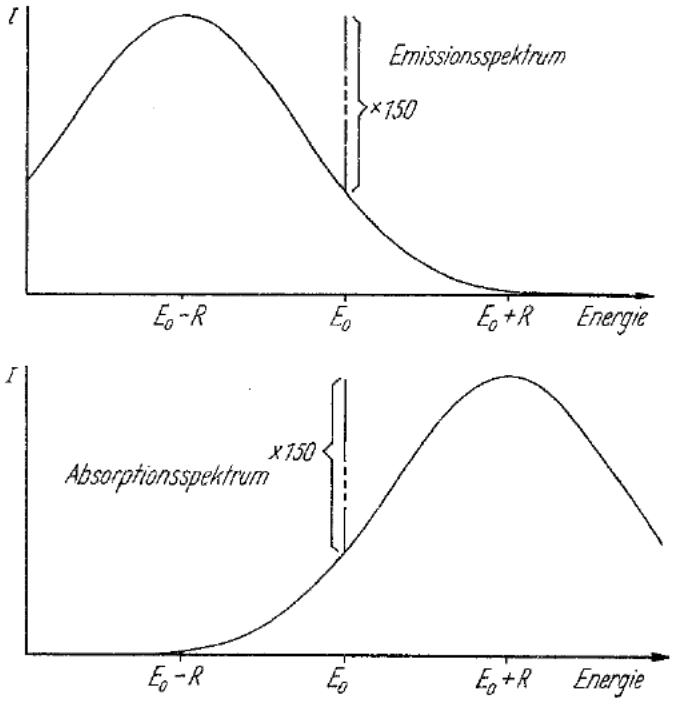


http://www.digitalclaritygroup.com/sales-success-knowing-audience/

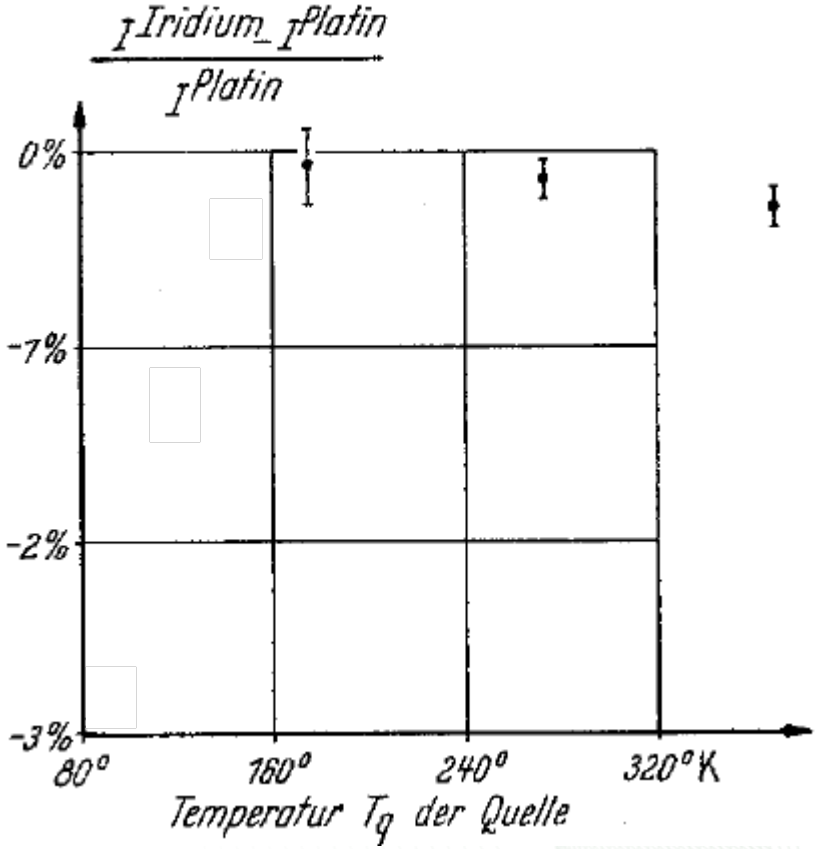
Nuclear resonant absorption?

„If the relative shift of the emission and the absorption lines resulting from the recoil-energy losses is only of the order of magnitude of the line widths, not only an increase but also **a decrease in temperature can result in a measurable change** in the nuclear absorption. My **decision** between these two possibilities was made in favour of a **temperature decrease**. It was motivated essentially by the consideration that **at low temperature, effects of chemical binding would be more likely** than at elevated temperatures."

R.L. Mössbauer, Nobel Lecture, The Nobel Foundation 1961



^{191}Ir E_0 = 129 keV



R. Mößbauer, Zeitschrift für Physik, 1958, 151, pp 124-143.

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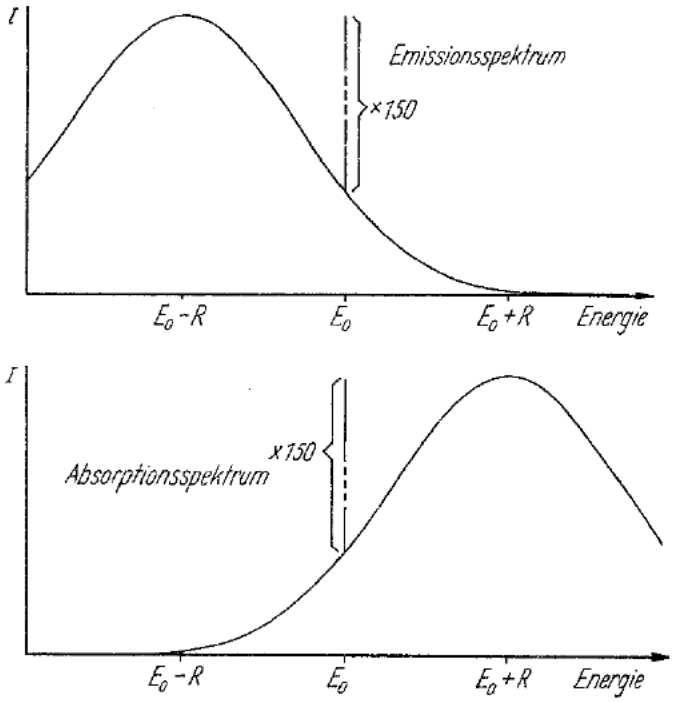

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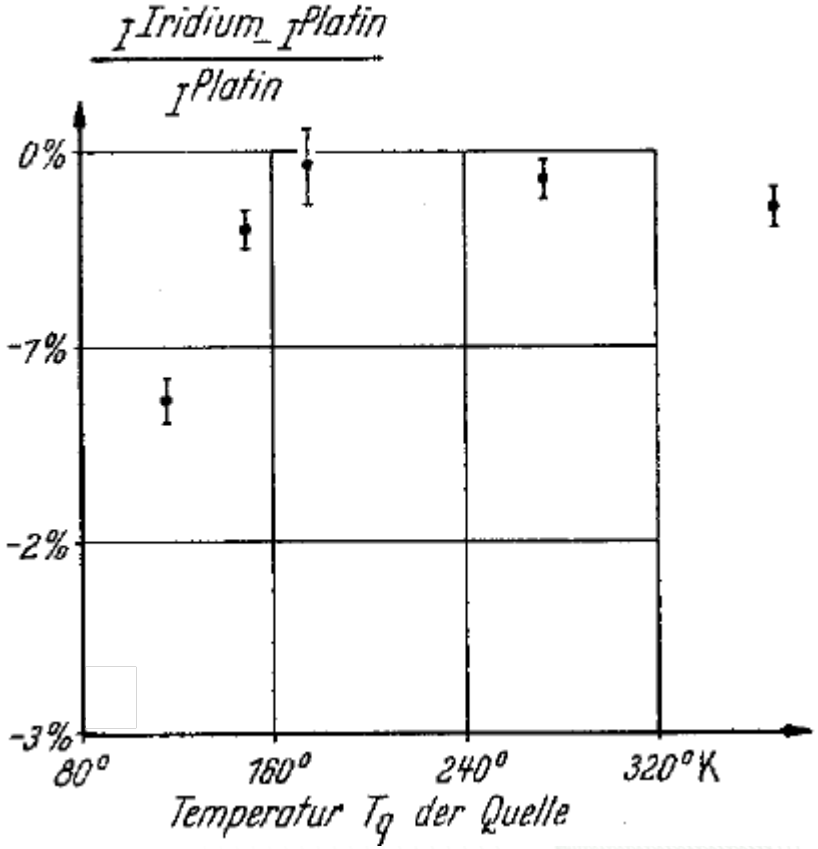

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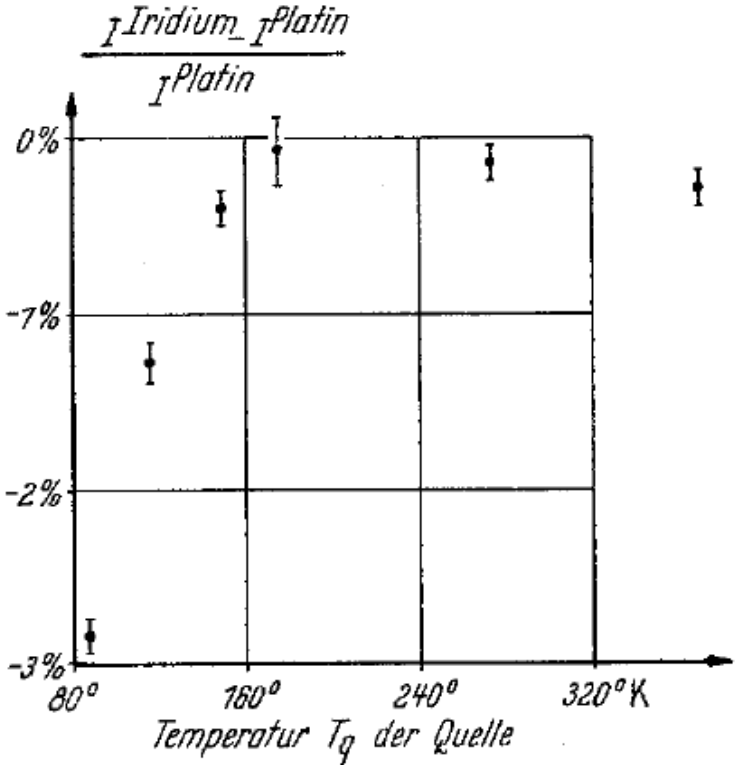

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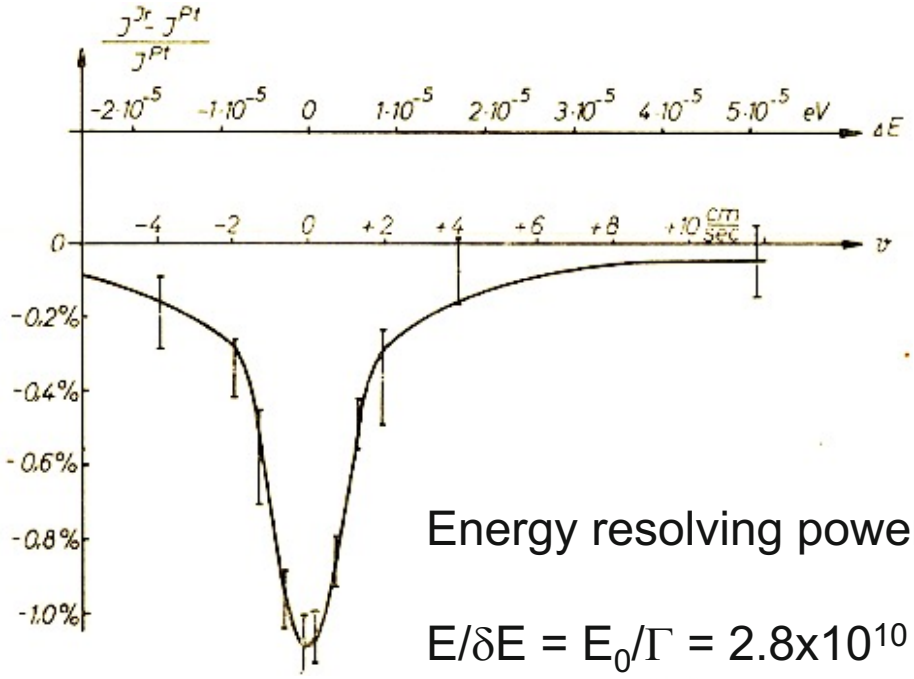


Energy resolving power:

$E/\delta E = E_0/\Gamma = 2.8 \times 10^{10}$

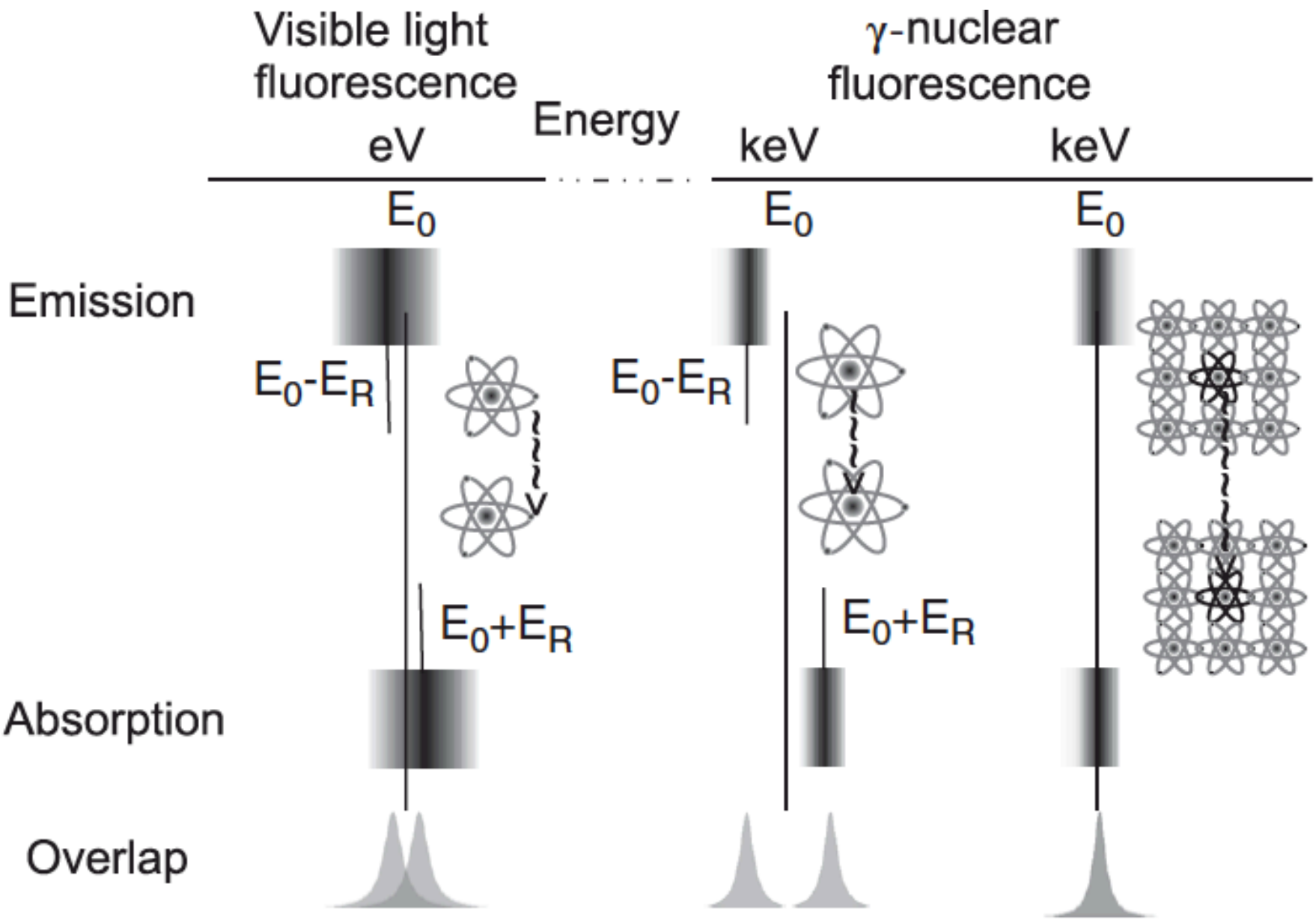
R.L. Mößbauer, Naturwiss. 45, 538 (1958)
R.L. Mößbauer, Z. Naturforsch. 14a, 211 (1959)

„Recoilless absorption and emission of gamma-rays“

„It is this property of the recoilless nuclear resonance absorption – namely, that it is possible by this means to measure extraordinarily small energy differences between two systems – which gave the method its significance and opened up a broad field of possible applications. Thus, the **extraordinary sharpness of the recoilless gamma lines** brought direct investigation of the **hyperfine structure** of nuclear transitions within the range of possibility.“

The Mößbauer effect

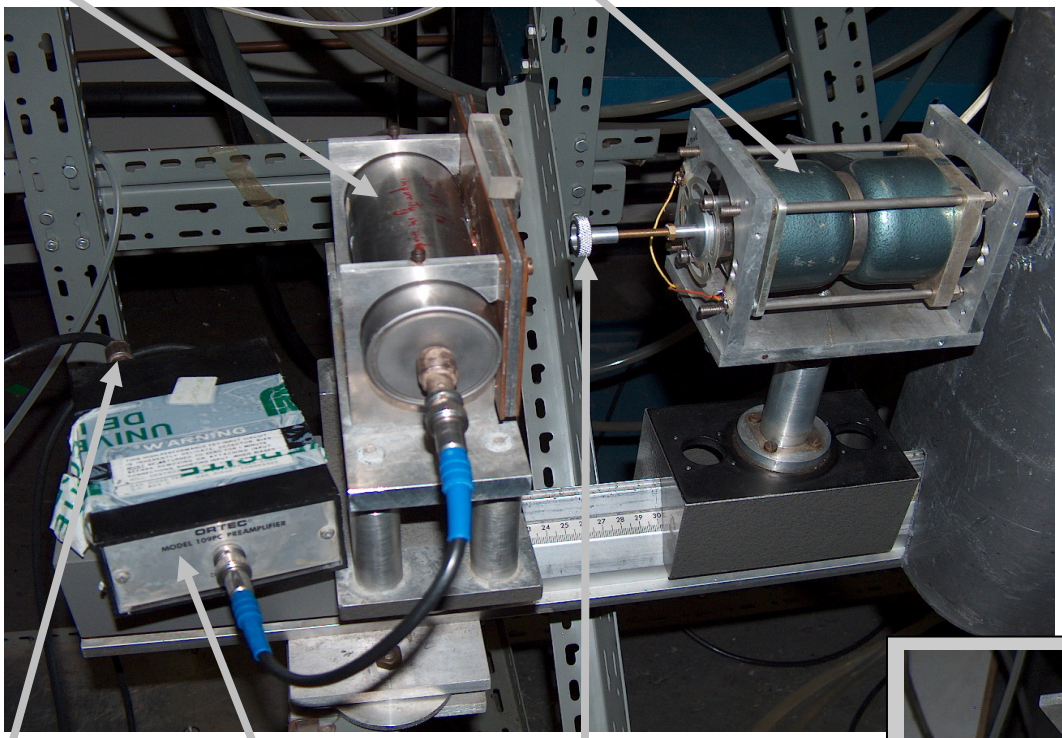
Summary

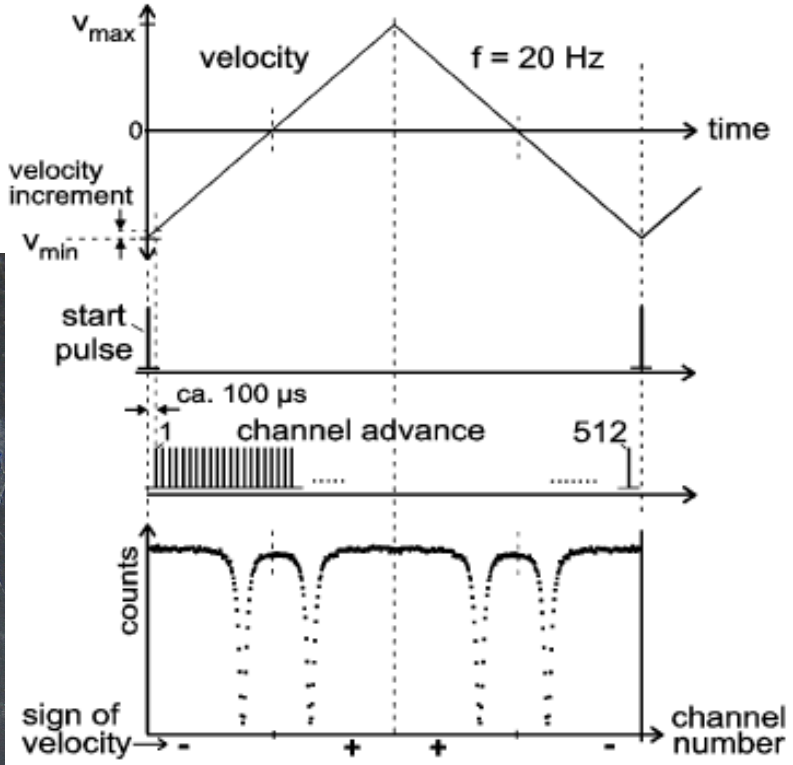

Visible light fluorescence
eV
Energy
γ-nuclear fluorescence
keV
keV
E0
E0
E0
Emission
E0-ER
E0-ER
E0+ER
E0+ER
Absorption
Overlap

Mößbauer spectroscopy: experimental setup

Drive and pickup coils

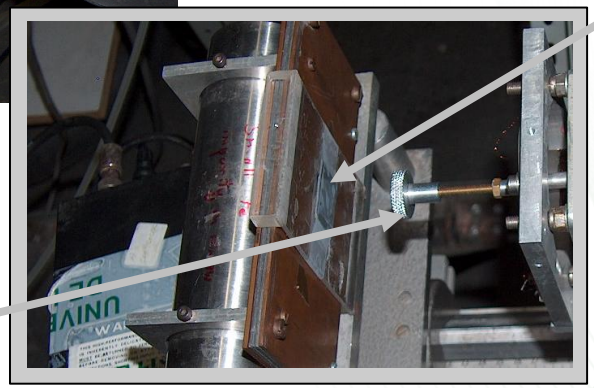
Detector





Gütlich, Bill, Trautwein (eds.), 2011.

Sample



to amplifier and MCA

Preamplifier

γ-ray source (*e.g.* ^{57}Co, ^{151m}Sm, ^{121m}Sn, ...)

Applications from fundamental physics to materials

Testing general relativity

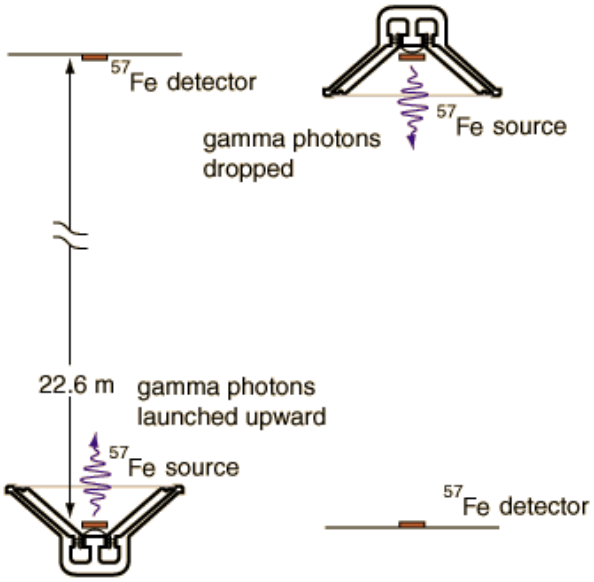
APPARENT WEIGHT OF PHOTONS*

R. V. Pound and G. A. Rebka, Jr.
Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts
(Received March 9, 1960)

$$(\Delta\nu)_{exp}/(\Delta\nu)_{theor} = +1.05 \pm 0.10,$$

$$\Delta E = mgh = \frac{E}{c^2}gh = \frac{14.4keV}{c^2}g \cdot 22.6m$$

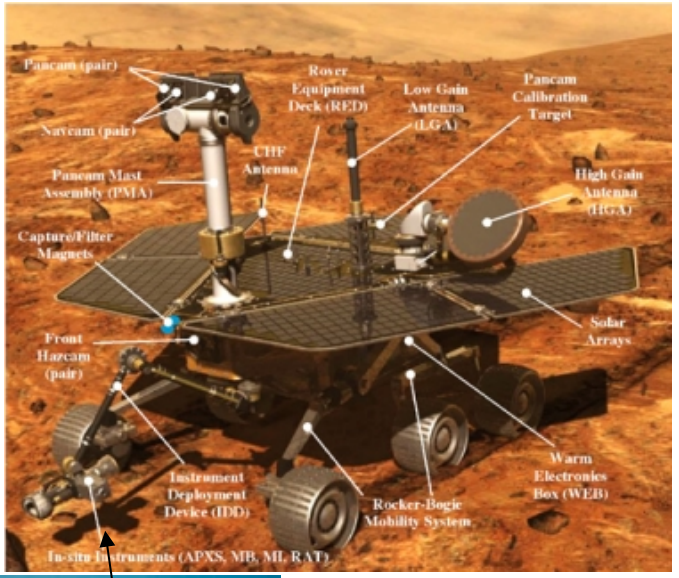
$$\Delta E = 3.5x10^{-11}eV$$

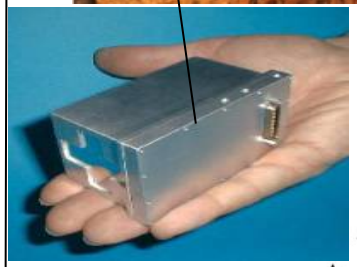


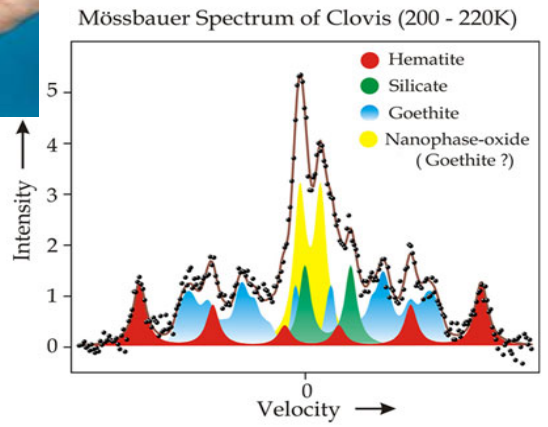
$$\left(\frac{\Delta E}{E}\right)_{down} - \left(\frac{\Delta E}{E}\right)_{up} = (5.1 \pm 0.5)x10^{-15}$$

http://hyperphysics.phy-astr.gsu.edu/hbase/relativ/gratim.html#c2

Mössbauer spectroscopy on Mars



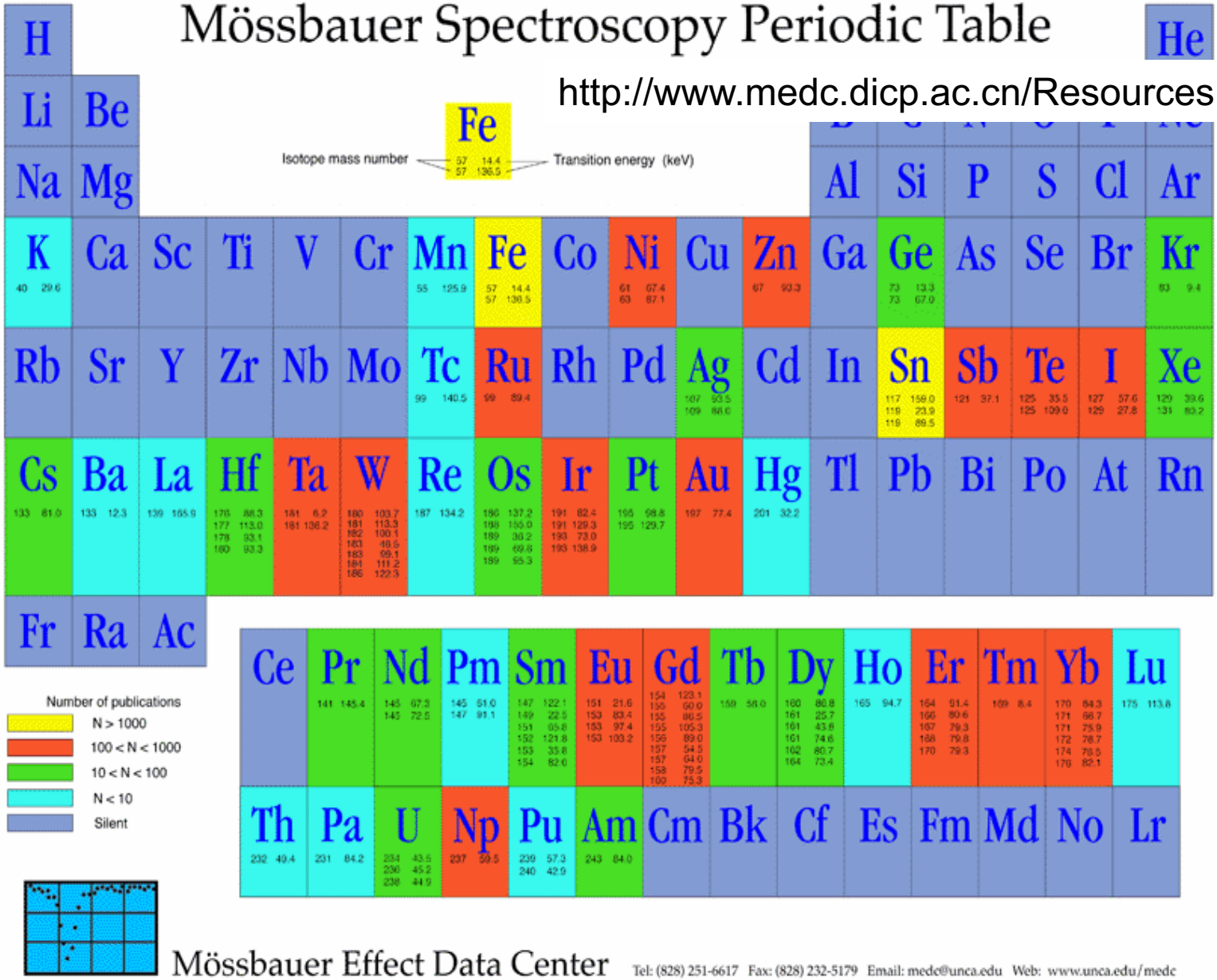




http://iacgu7.chemie.uni-mainz.de/klingelhoefer/

Personally: a piece from the Titanic, steel from Caterpillar, pottery, soil – climate research, soil – gas and oil industry, glass (green, brown, tin-float), cancer therapy complexes, pigments, …

Rule 1: Know your audience



Common *vs* uncommon transitions

Nuclide	E_0 (keV)	τ_0(ns)	a(%)	I_g	I_e	α	σ_n/kbarn	σ_n/σ_{ph}
^{187}Os	9.777	3.43	1.6	$1/2^-$	$3/2^-$	264.	194.4	5.84
^{57}Fe	14.4129	141.	2.14	$1/2^-$	$3/2^-$	8.18	2464.0	428.58
^{151}Eu	21.5412	14.0	47.8	$5/2^+$	$7/2^+$	28.0	242.6	29.06
^{149}Sm	22.5015	10.3	13.8	$7/2^-$	$5/2^+$	29.2	120.1	17.29
^{119}Sn	23.8793	25.6	8.58	$1/2^+$	$3/2^+$	5.22	1380.5	562.59
^{125}Te	35.4920	2.14	6.99	$1/2^+$	$3/2^+$	14.0	259.0	44.11
^{121}Sb	37.1292	4.99	57.3	$5/2^+$	$7/2^+$	11.11	195.4	40.26
^{129}Xe	39.5813	1.47	26.4	$1/2^+$	$3/2^+$	12.31	234.7	47.24
^{61}Ni	67.408	7.60	1.19	$3/2^-$	$5/2^-$	0.139	709.1	7046.
^{73}Ge	68.752	2.51	7.76	$9/2^+$	$7/2^+$	0.227	337.5	2121.
^{197}Au	77.351	2.76	100.	$3/2^+$	$1/2^+$	4.36	38.1	56.22
^{191}Ir	82.407	5.89	37.3	$3/2^+$	$1/2^+$	10.9	15.1	6.20
^{155}Gd	86.546	9.13	14.7	$3/2^-$	$5/2^+$	0.434	341.7	304.61
^{99}Ru	89.571	28.8	12.7	$5/2^+$	$3/2^+$	1.498	81.2	315.04

R. Hermann, *Mössbauer Spectroscopy*, p.443-484, in Handbook of Solid State Chemistry, Eds. Dronskowski, Kikkawa, and Stein, 2017 Wiley-VCH

- Historical perspective
- Spectral description and parameters
- Static interactions
- Time dependent interactions

Lattice dynamics

Probability for recoilless absorption of emission of gamma-rays:

Lamb-Mössbauer factor: $f = \exp\left[-\langle x^2 \rangle E_\gamma^2 / (\hbar c)^2\right]$

Single particle – incoherent – absorption

In a solid the recoil is distributed to the crystal → negligible as $M >> m_{nucleus}$

and to the lattice vibrations → quantized in phonons.

The Lamb-Mössbauer factor quantifies the 0-phonon probability.

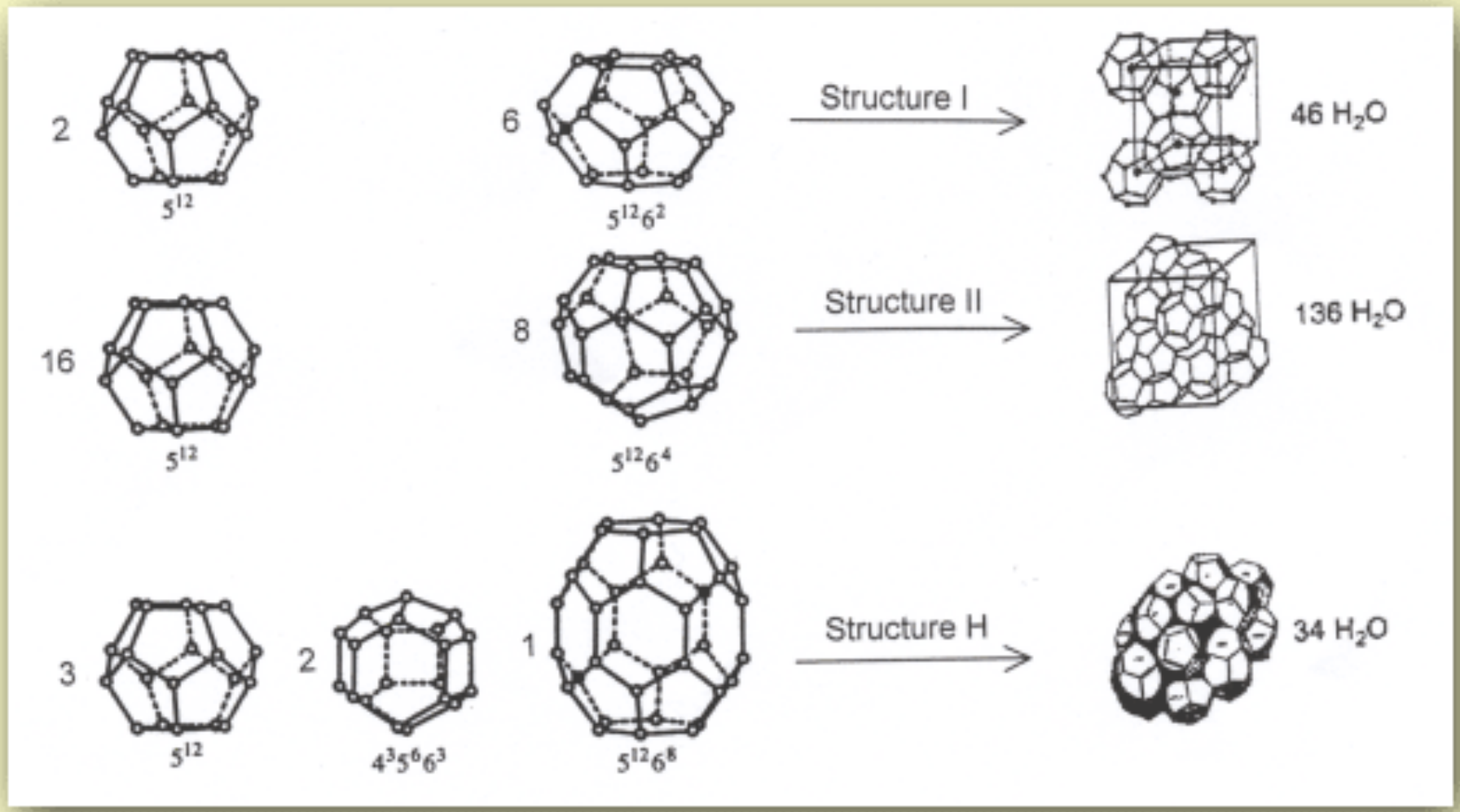
$$f_{DW} = exp(- < \mathbf{u}.\mathbf{q} >^2)$$

$|\mathbf{q}| = 4\pi \sin\theta/\lambda$

Similar, but not to be confused with the Debye-Waller factor:

Pair distribution function – coherent – scattering

Guest dynamics in clathrates



http://www.calstatela.edu/dept/chem/ba/researchtops-gashy.htm

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Guest dynamics in clathrates

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 49, NUMBER 4 15 AUGUST 1968

Dynamics of Krypton Atoms in Clathrate by the Mössbauer Technique*

Y. HAZONY

Department of Chemical Engineering, Princeton University, Princeton, New Jersey

AND

S. L. RUBY

Physics Division, Argonne National Laboratory, Argonne, Illinois

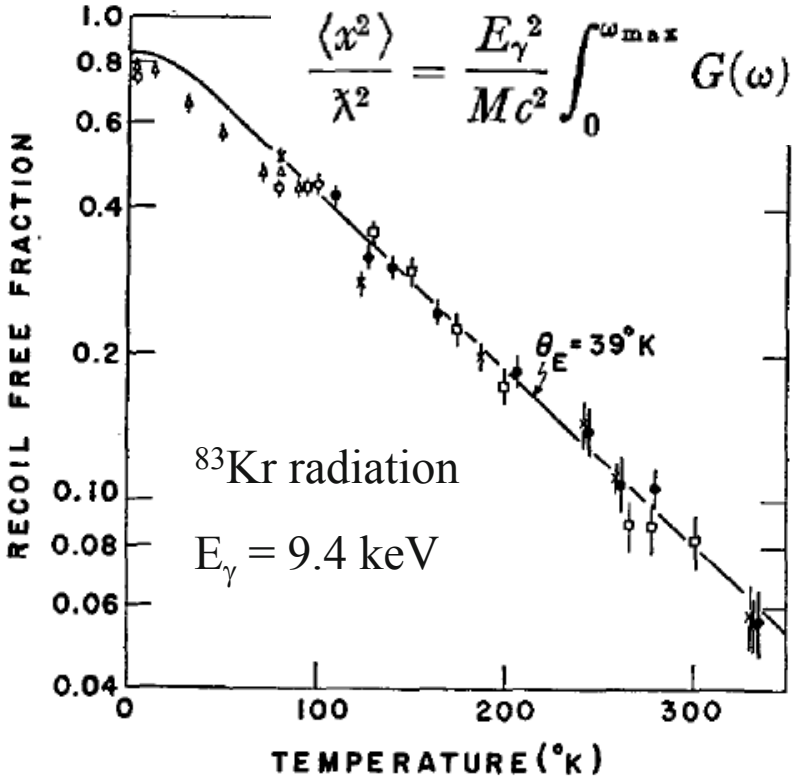


FIG. 1. Experimental results for the recoil-free fraction f vs temperature for Kr in HQ clathrate. The solid curve is that calculated for a particle in a harmonic well, for which $x^2/\lambda\!\!\!^{-2} = (E^2/2mc^2)\,(k\theta)^{-1}(1+e^{-u})\,(1-e^{-u})^{-1}$, $\mu = \Theta/T$, $\theta = 39°\text{K}$.

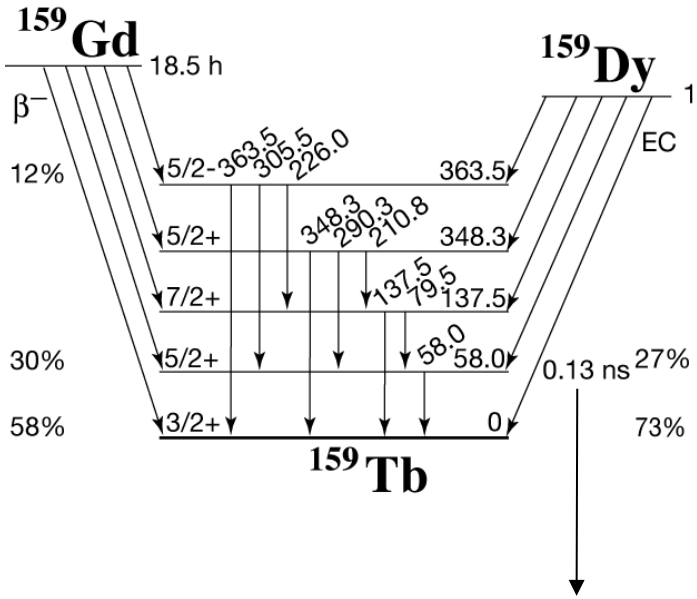
The hydroquinone (HQ) clathrate structure provides a solid "cagework" in which a variety of atoms or even small molecules may be trapped.[1] Since the guest atoms and molecules are confined mainly by the repulsive forces of the walls of the cages, this structure has been considered as an ideal case for the study of the cell model, which is used in statistical thermodynamics to describe the behavior of liquid and solid solutions. A large amount of experimental and theoretical work has been performed on the dynamics of the trapped molecules as well as on the nature of their interaction with the walls.

The theoretical analysis of the thermodynamic properties of these compounds is usually based on the cell model. In this approximation, the interaction between the trapped molecule and the cage is represented by a static potential well and the vibrations of the molecule in the cell are assumed to be completely decoupled from the dynamics of the host lattice as well as from the other guest molecules in the adjacent cells.[2]

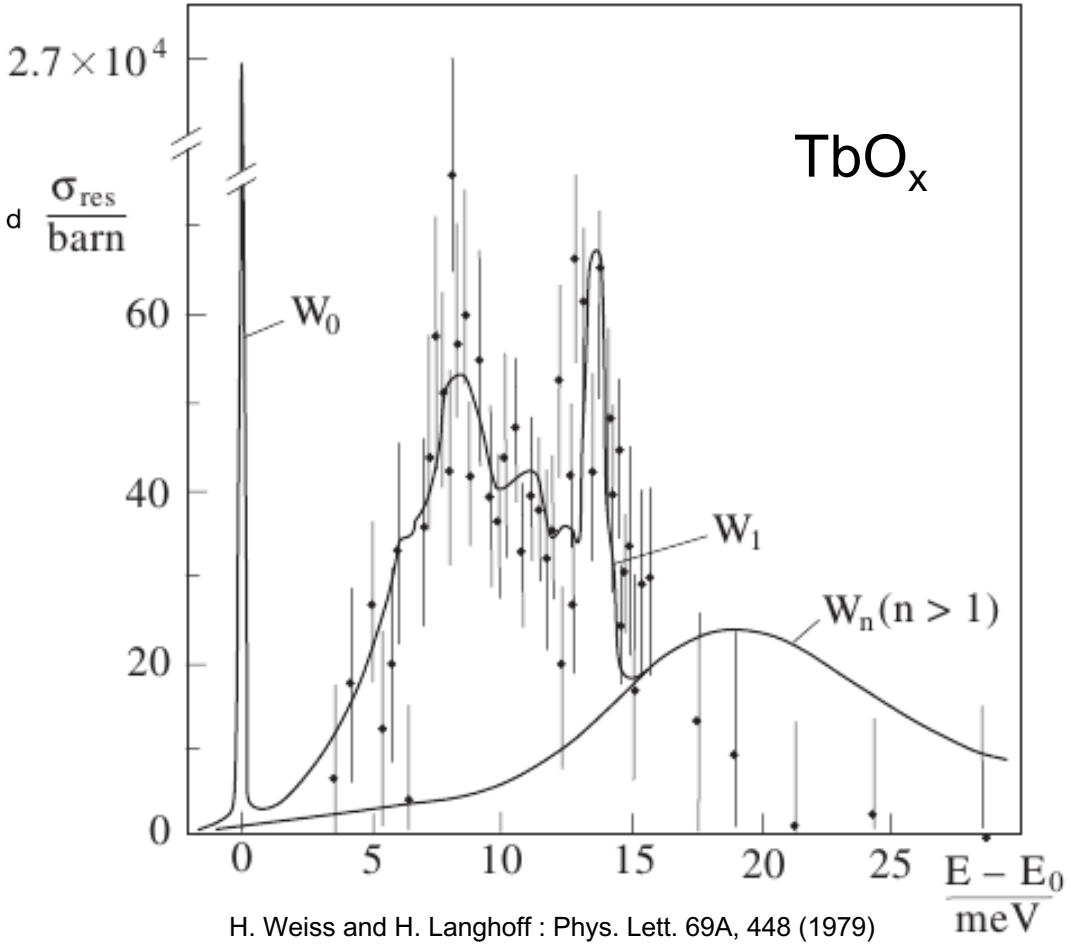
Accessing phonon modes

If Doppler velocity is increased:

$$E - E_0 = E_0 . v/c \sim 16.7 \text{ meV, for 100 m/s and } E_0 = 50 \text{ keV}$$

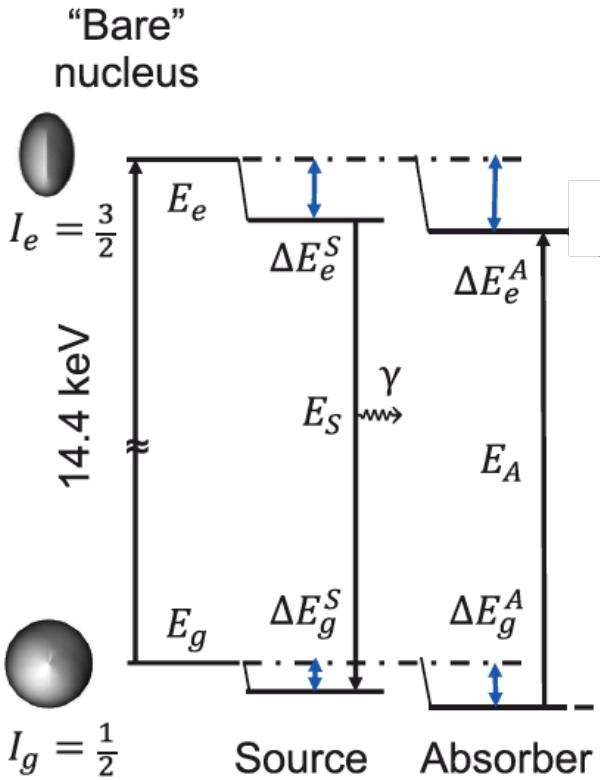


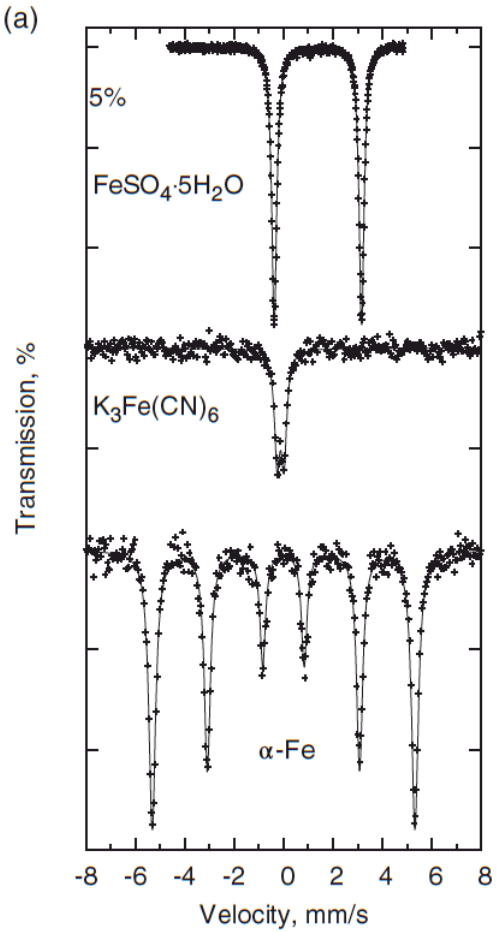
Heisenberg relation: $\Gamma = 5\ \mu eV$



H. Weiss and H. Langhoff : Phys. Lett. 69A, 448 (1979)

Electric monopole: isomer shift





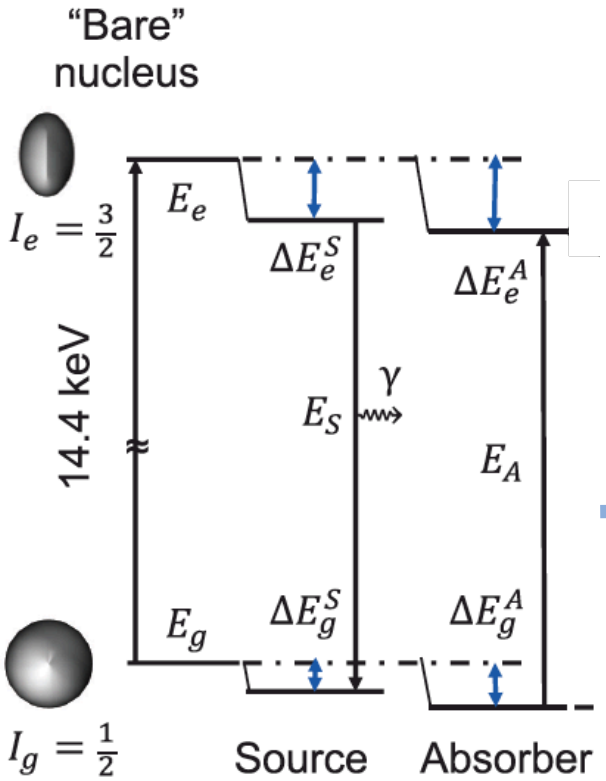
$$\delta = E_S - E_A = (\Delta E_e^S - \Delta E_g^S) - (\Delta E_e^A - \Delta E_g^A)$$

Isomer shift

Sample property

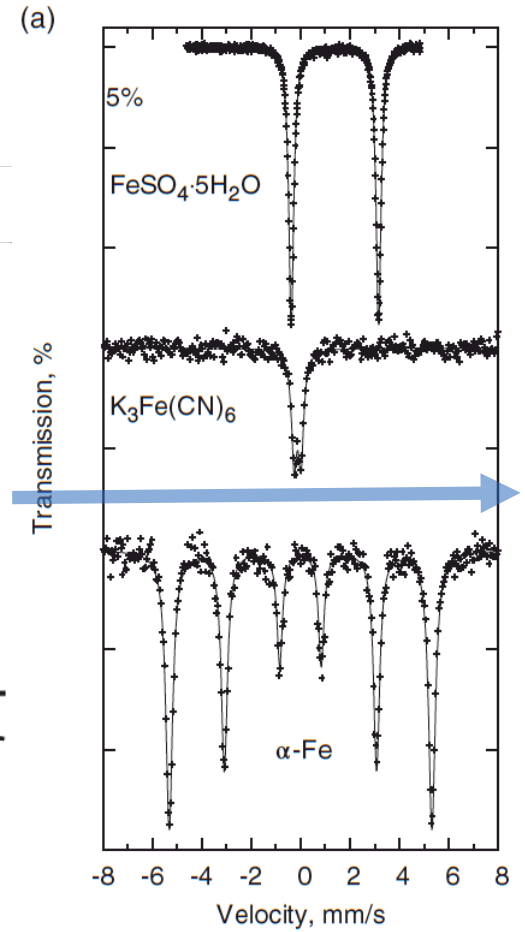
$$\delta = E_A - E_S = \frac{2\pi}{5} Ze^2(\rho_A(0) - \rho_S(0))\left[R_e^2 - R_g^2\right]$$

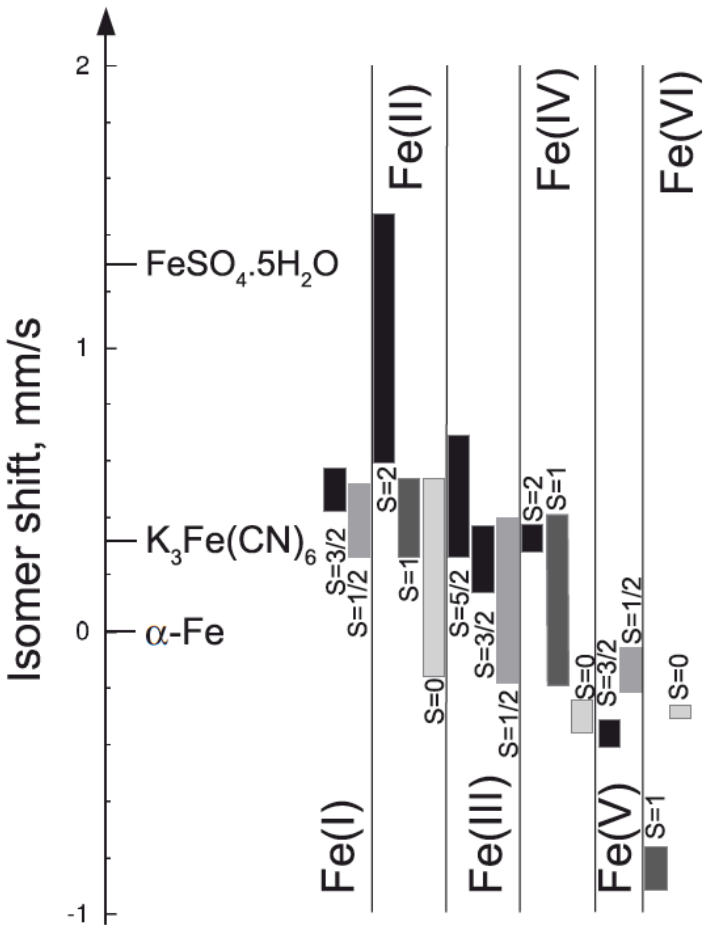
Electric monopole: isomer shift



$$\delta = E_S - E_A = \left(\Delta E_e^S - \Delta E_g^S\right) - \left(\Delta E_e^A - \Delta E_g^A\right)$$

Isomer shift





Sample property

$$\delta = E_A - E_S = \frac{2\pi}{5} Ze^2 \left(\rho_A(0) - \rho_S(0)\right)\left[R_e^2 - R_g^2\right]$$

TEMPERATURE-DEPENDENT SHIFT OF γ RAYS EMITTED BY A SOLID

B. D. Josephson
Trinity College, Cambridge, England
(Received March 11, 1960)

Recent experiments by Mössbauer[1] have shown that when low-energy γ rays are emitted from nuclei in a solid a certain proportion of them are unaffected by the Doppler effect. It is the purpose of this Letter to show that they are nevertheless subject to a temperature-dependent shift to lower energy which can be attributed to the relativistic time dilatation caused by the motion of the nuclei.

Let us regard the solid as a system of interacting atoms with the Hamiltonian

$$H = \sum p_i^2/2m_i + V(r_1, r_2, \cdots).$$

The Mössbauer effect is due to those processes in which the phonon occupation numbers do not change. It might appear that in such cases the energy of the solid is unaltered, but this is not so, as the nucleus which emits the γ ray changes its mass, and this affects the lattice vibrations. Suppose the nucleus of the ith atom emits a γ ray of energy E, its mass changing by $\delta m_i = -E/c^2$.

The change in energy, δE, of the solid is given by

$$\delta E = \langle \Delta H \rangle = \delta \langle p_i^2/2m_i \rangle = -\delta m_i \langle p_i^2/2m_i^2 \rangle$$

$$= (\delta m_i/m_i) T_i = (E/m_i c^2) T_i,$$

where T_i is the expectation value of the kinetic energy of the ith atom. The energy of the γ ray must accordingly be reduced by δE so there is a shift of relative magnitude $\delta E/E = T_i/m_i c^2$. The same formula can be deduced by regarding the shift as due to a relativistic time dilatation.

To estimate T_i we make the following assumptions: (i) The atoms all have the same mass, and the kinetic energy is equally distributed among them. (ii) The kinetic energy is half the total lattice energy, i.e., we assume that the forces coupling the atoms are harmonic. Under these assumptions $T_i/m_i = \frac{1}{2}U$, where U is the lattice energy per unit mass. The relative shift is thus given by $\delta E/E = U/2c^2$. For Fe at 300°K

this has the value 8×10^{-13}. Clearly a compensating shift would occur for absorption provided source and absorber were identical and at the same temperature. A small difference in temperature between source and absorber leads to a relative shift per degree given by $\delta E/E = C_p/2c^2$ where C_p is the specific heat. For Fe at 300°K this is 2.2×10^{-15}/°K. This is sufficient for it to be necessary to take it into account in accurate experiments using the resonance absorption of γ rays, such as those to measure the gravitational red shift.[2,3]

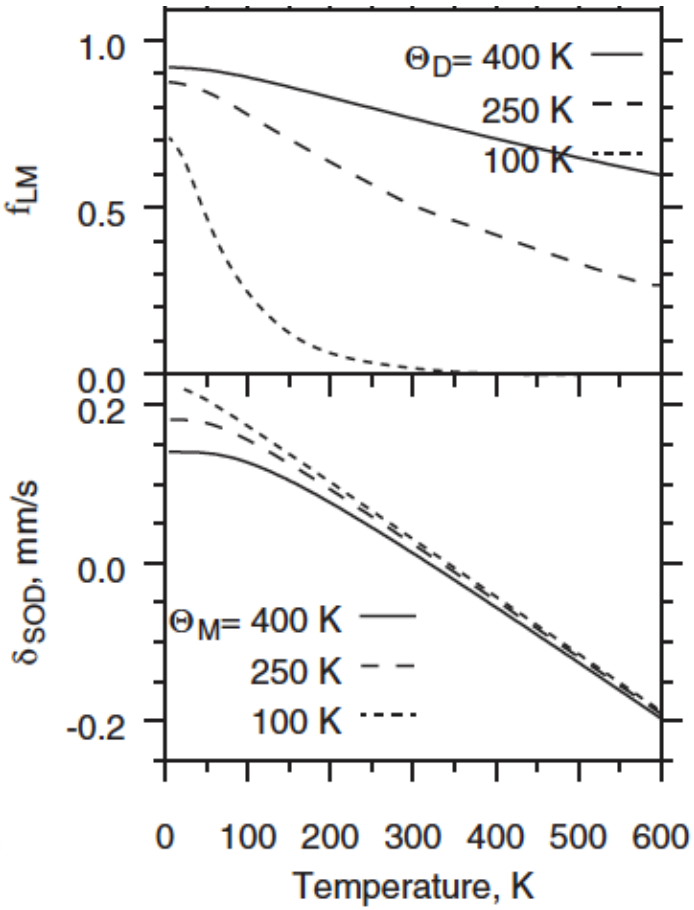
I would like to thank Dr. Ziman, Professor O. R. Frisch, and Dr. W. Marshall for helpful discussions.

[1] R. L. Mössbauer, Z. Physik 151, 124 (1958).
[2] R. V. Pound and G. A. Rebka, Phys. Rev. Letters 3, 554 (1959).
[3] T. E. Cranshaw, J. P. Schiffer, and A. B. Whitehead, Phys. Rev. Letters 4, 163 (1960).

UPPER LIMIT FOR THE ANISOTROPY OF INERTIAL MASS FROM NUCLEAR RESONANCE EXPERIMENTS*

V. W. Hughes, H. G. Robinson, and V. Beltran-Lopez
Gibbs Laboratory, Yale University, New Haven, Connecticut
(Received March 2, 1960)

$$f_{LM} = \exp\left(-k^2 . \langle x^2 \rangle\right)$$



$$\delta_{SOD} = -\langle v^2 \rangle / 2c$$

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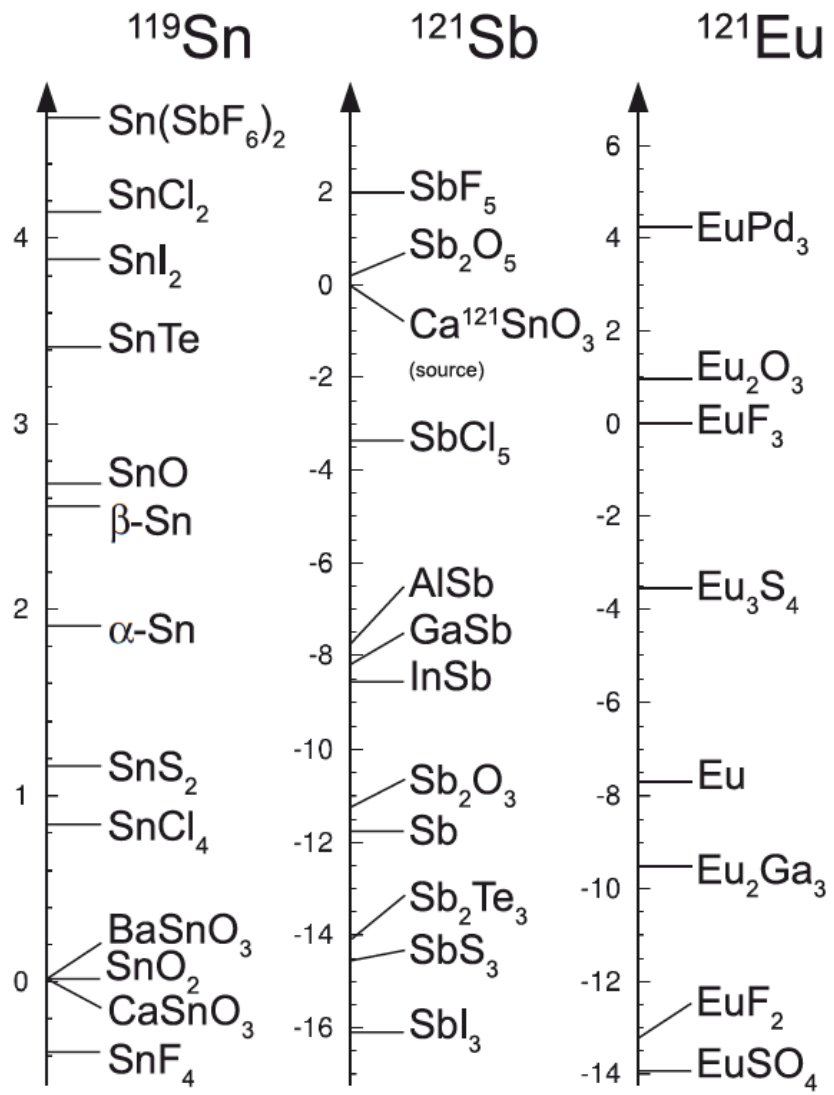
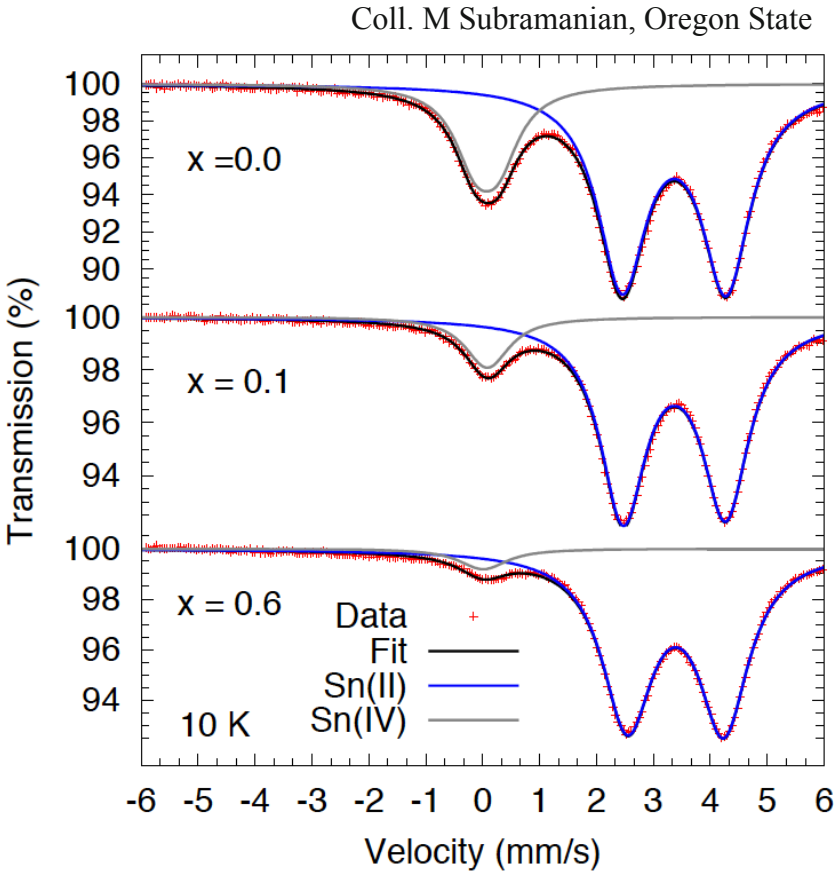
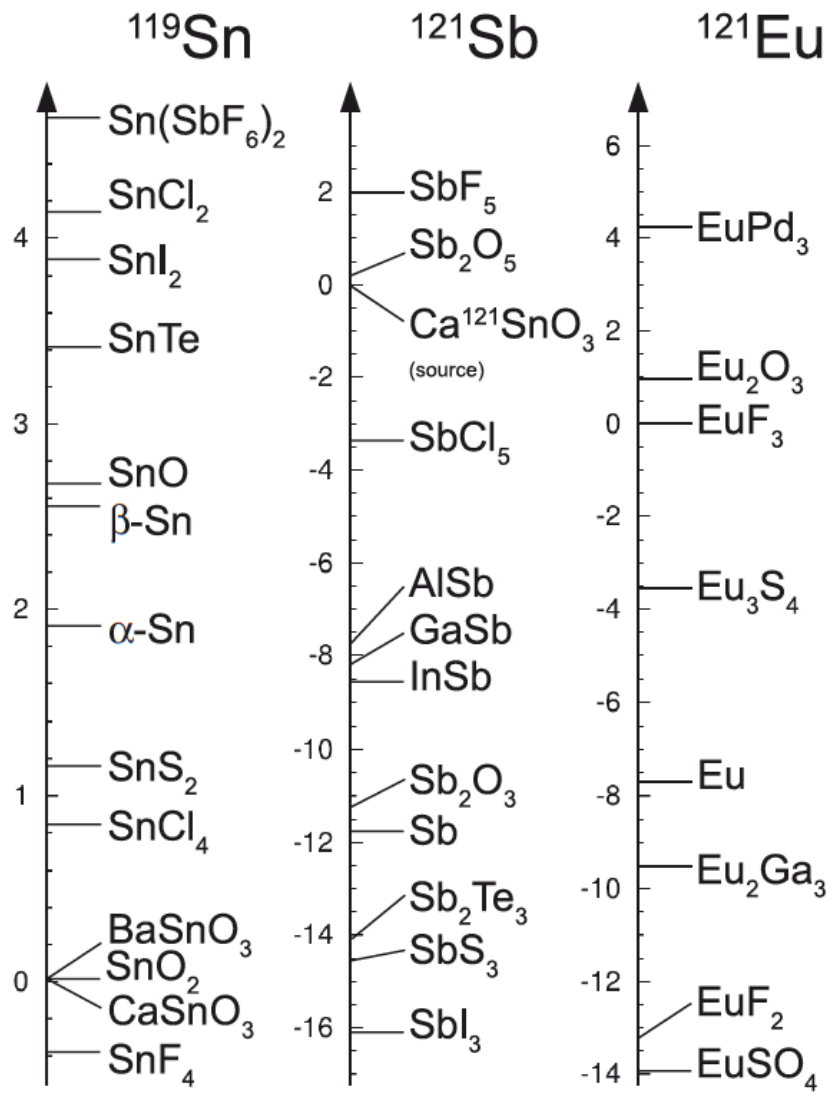
Electric monopole: isomer shift



$Sn_2Nb_2O_{7-x}S_x$

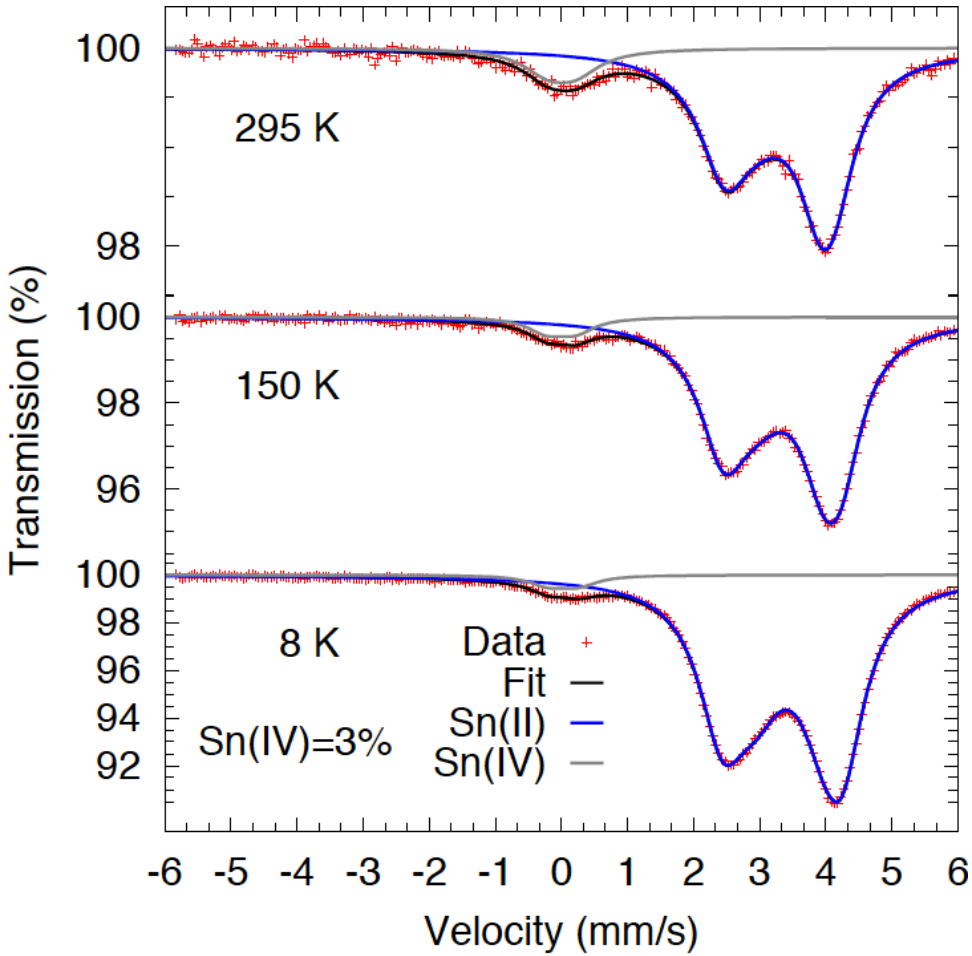


Atomic fractions: temperature dependence



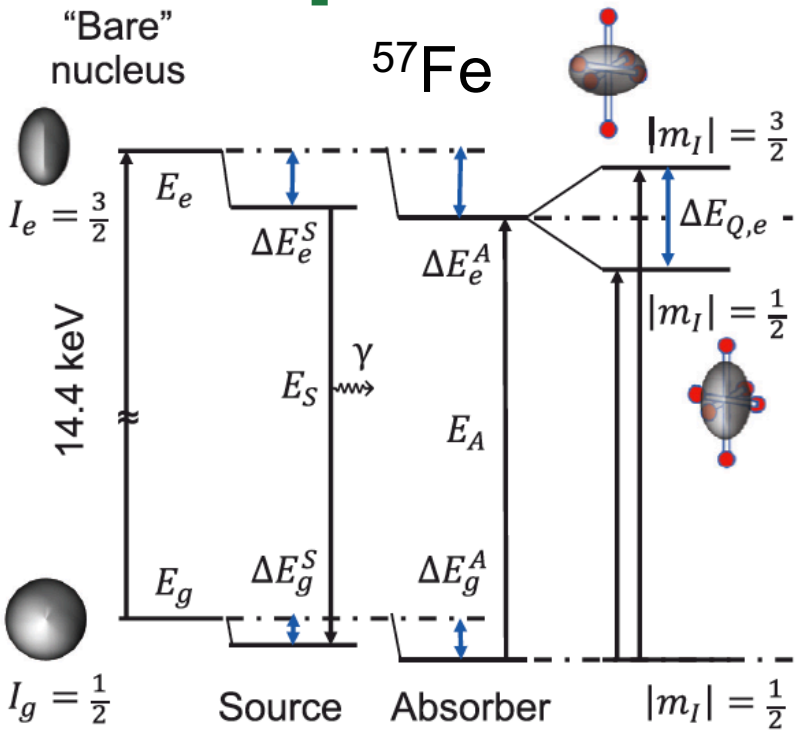
$Sn_2Nb_2O_6F$

Coll. M Subramanian, Oregon State

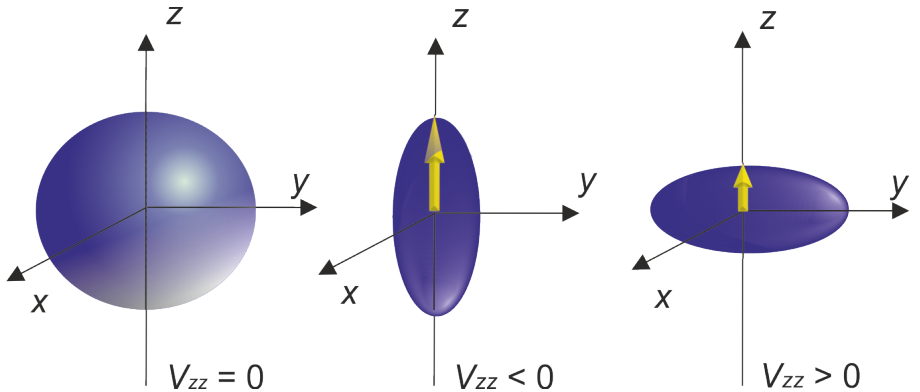


Quadrupole interaction

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$



$$\hat{\mathcal{H}}^Q_{(g,e)} = \sum_{i,j} Q^{ij} V_{ij} = \frac{eQ_{(g,e)}}{I \cdot (2I-1)} \left(V_{zz} . \hat{I}_z^2 + V_{yy} . \hat{I}_y^2 + V_{xx} . \hat{I}_x^2 \right)$$



http://www.advancedmaterialsgroup.edu.rs/wp-content/uploads/2013/07/Slika-1.2.1-EFG.png

$$E^Q_{g,e}(I, m_I) = \frac{eQ_{g,e} V_{zz}}{4I_{g,e} \cdot (2I_{g,e} - 1)} \left[3m_I^2 - I.(I+1) \right] \sqrt{(1 + \eta^2/3)}$$

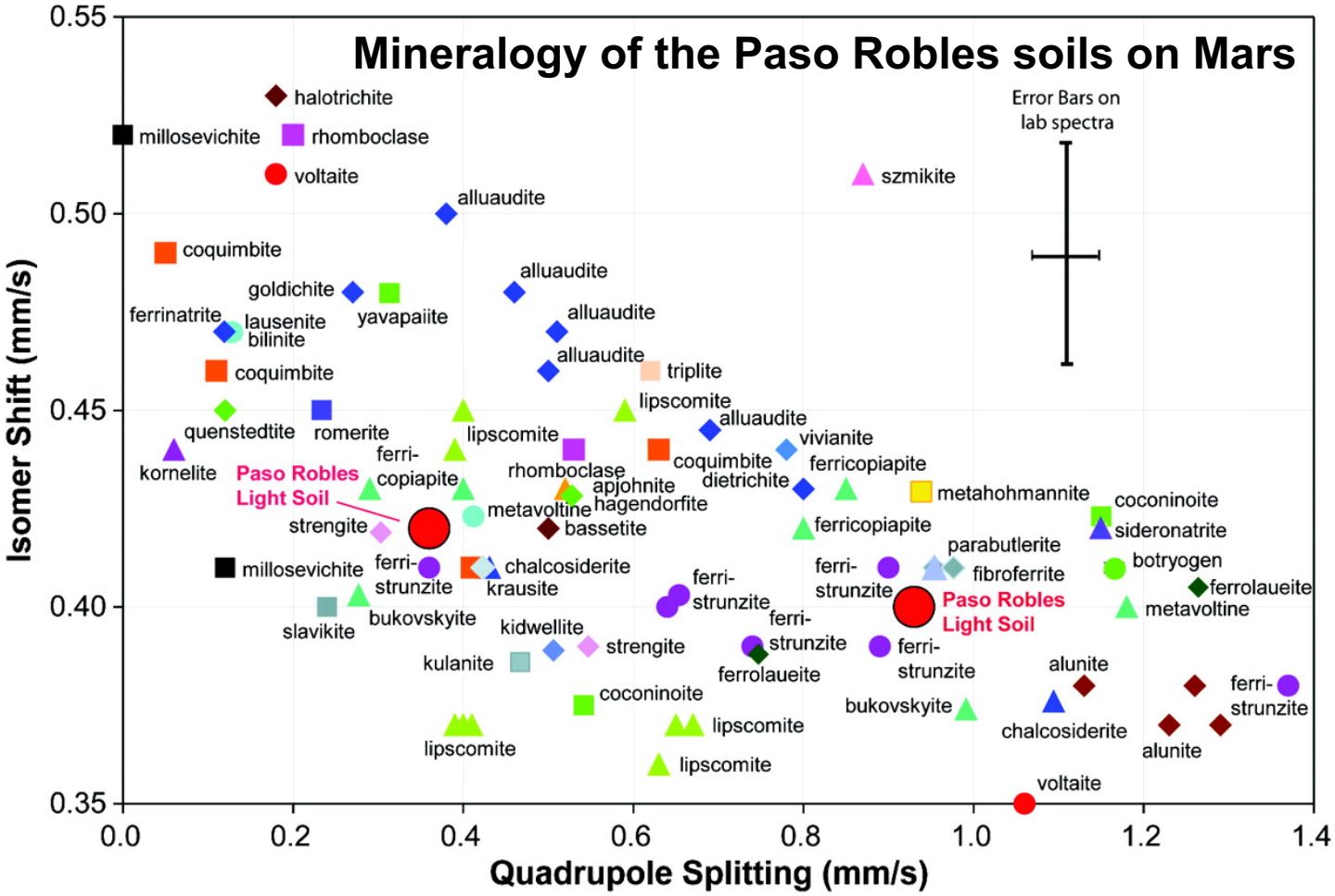
1) Lattice contribution → point symmetry + point charges located on surrounding atoms.

2) Valence electron contribution → crystal field + orbital term (essential for transition metals)

Isomer shift vs. quadrupole splitting

Mössbauer fingerprinting

http://ammin.geoscienceworld.org/content/93/5-6/728

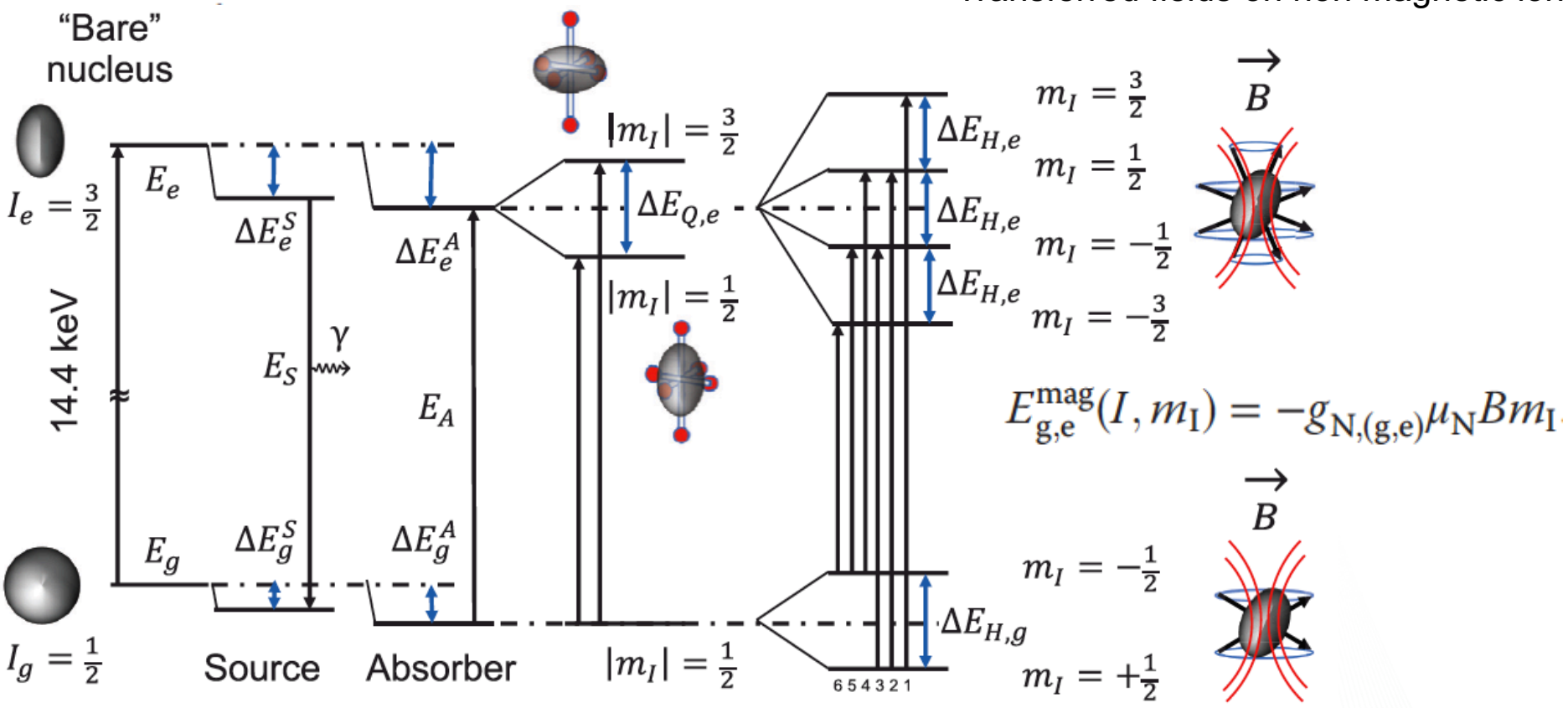


M.D. Lane *et al.*, Amer. Mineralogist **93** no. 5-6 728-739

Magnetic Zeeman interaction

$$\hat{\mathcal{H}}^{\text{mag}}_{(g,e)} = -\hat{\mu}\cdot\hat{\mathbf{B}} = -g_{N,(g,e)}\mu_N\hat{\mathbf{I}}\cdot\hat{\mathbf{B}}$$

- Magnetically ordered materials
- Applied magnetic field in diamagnets
- Transferred fields on non magnetic ions

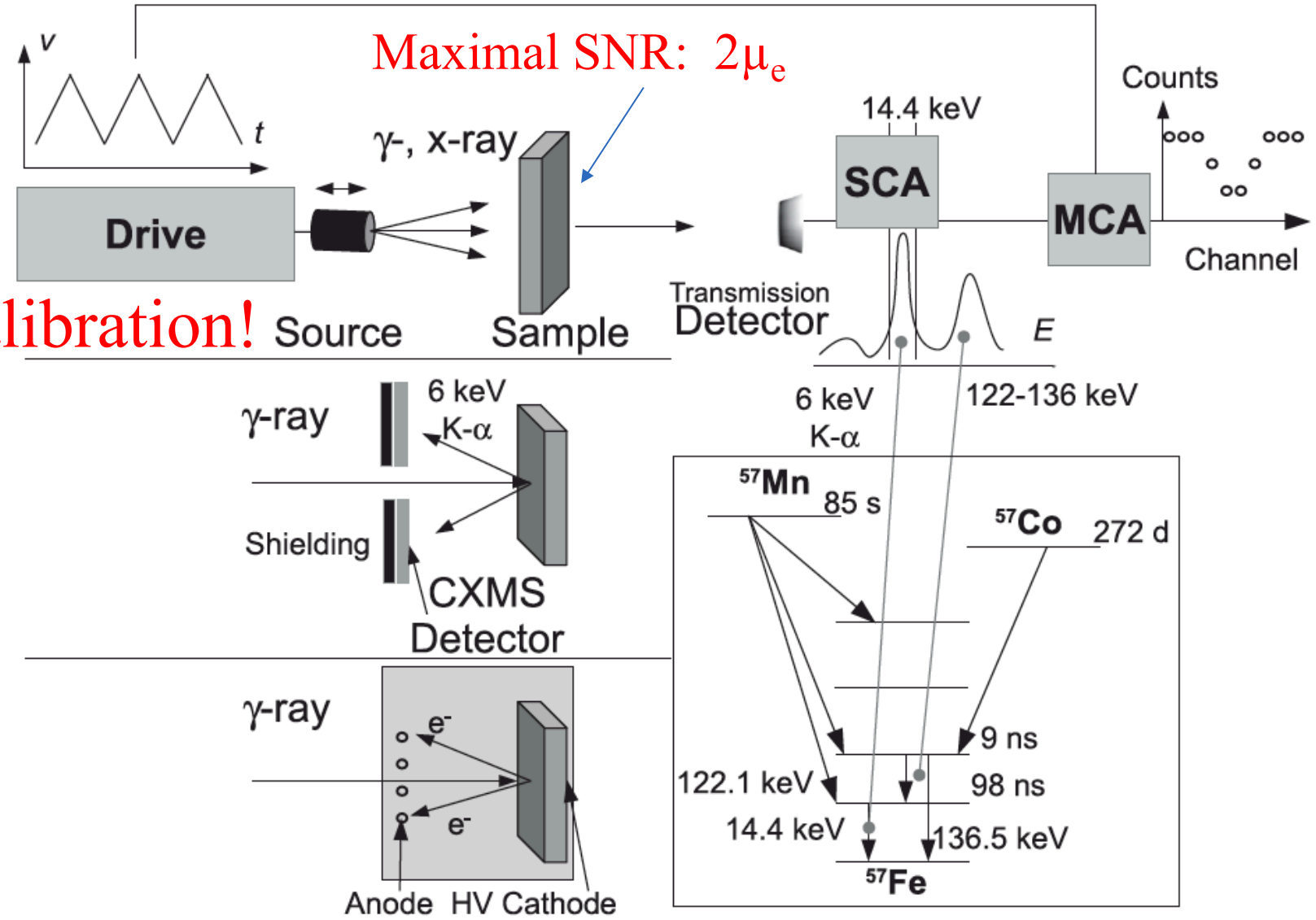


$$E^{\text{mag}}_{g,e}(I, m_I) = -g_{N,(g,e)}\mu_N B m_I$$

$$\delta = E_S - E_A = \left(\Delta E_e^S - \Delta E_g^S\right) - \left(\Delta E_e^A - \Delta E_g^A\right)$$

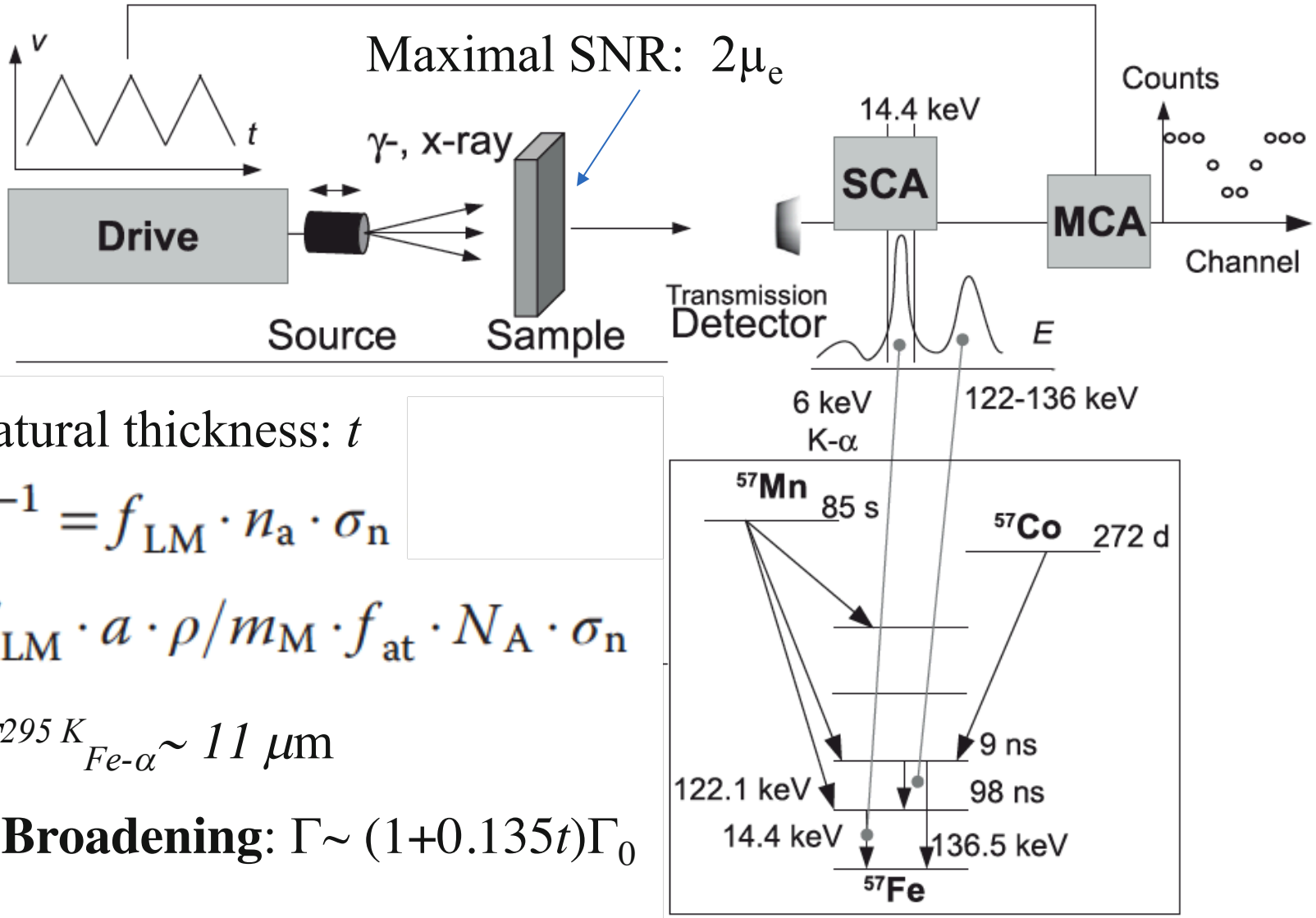
Isomer shift | Quadrupole splitting | Magnetic hyperfine splitting

Technique and optimization



$$t^{-1} = f_{\mathrm{LM}} \cdot n_{\mathrm{a}} \cdot \sigma_{\mathrm{n}} = f_{\mathrm{LM}} \cdot a \cdot \rho / m_{\mathrm{M}} \cdot f_{\mathrm{at}} \cdot N_{\mathrm{A}} \cdot \sigma_{\mathrm{n}}$$

Technique and optimization



Natural thickness: t

$$t^{-1} = f_{\mathrm{LM}} \cdot n_{\mathrm{a}} \cdot \sigma_{\mathrm{n}}$$

$$= f_{\mathrm{LM}} \cdot a \cdot \rho / m_{\mathrm{M}} \cdot f_{\mathrm{at}} \cdot N_{\mathrm{A}} \cdot \sigma_{\mathrm{n}}$$

$T^{295\,K}_{Fe\text{-}\alpha} \sim 11\ \mu\mathrm{m}$

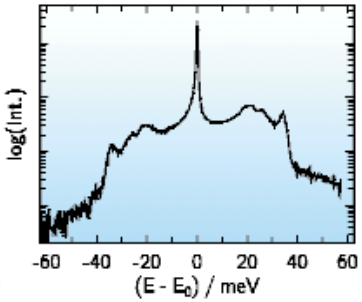
! Broadening: $\Gamma \sim (1+0.135t)\Gamma_0$

Choose wisely! -> e.g. programm mossthick

Nuclear resonance scattering

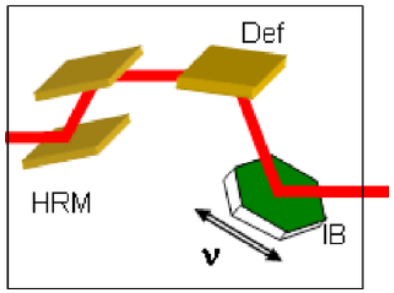
= Time or Energy Domain Synchrotron Mössbauer Spectroscopy
+ Phonon Assisted Nuclear Resonance Absorption
+ Synchrotron Radiation Perturbed Angular Correlation
+ …

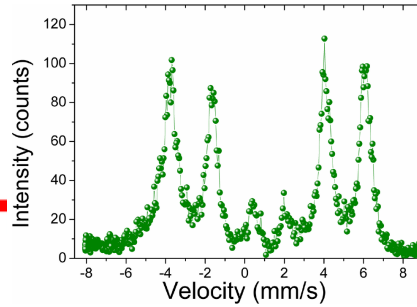
+ polarized beam.



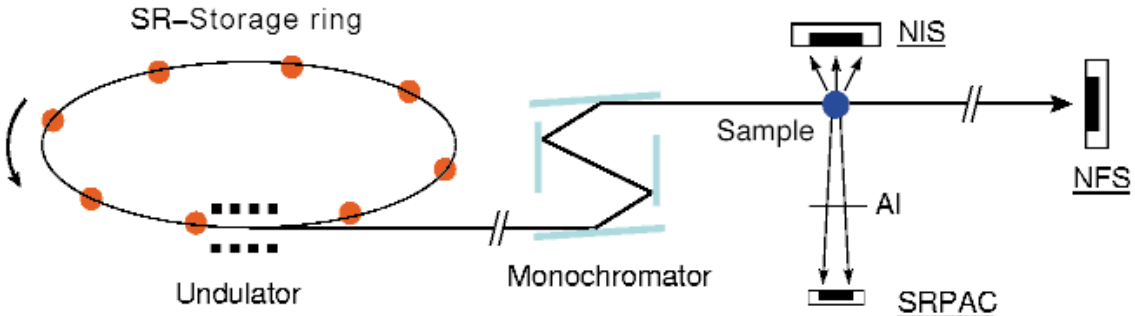
With recoil
→ inelastic

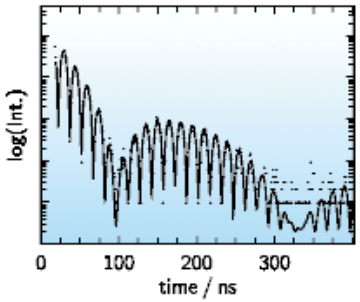
SMS



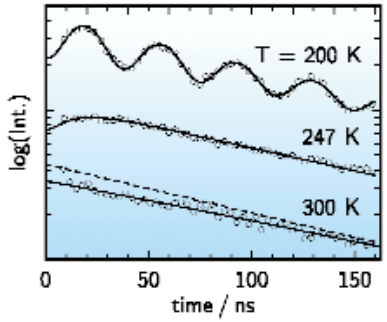


Potapkin et al. J. Synchrotron Rad. (2012). 19, 559–569





Without recoil

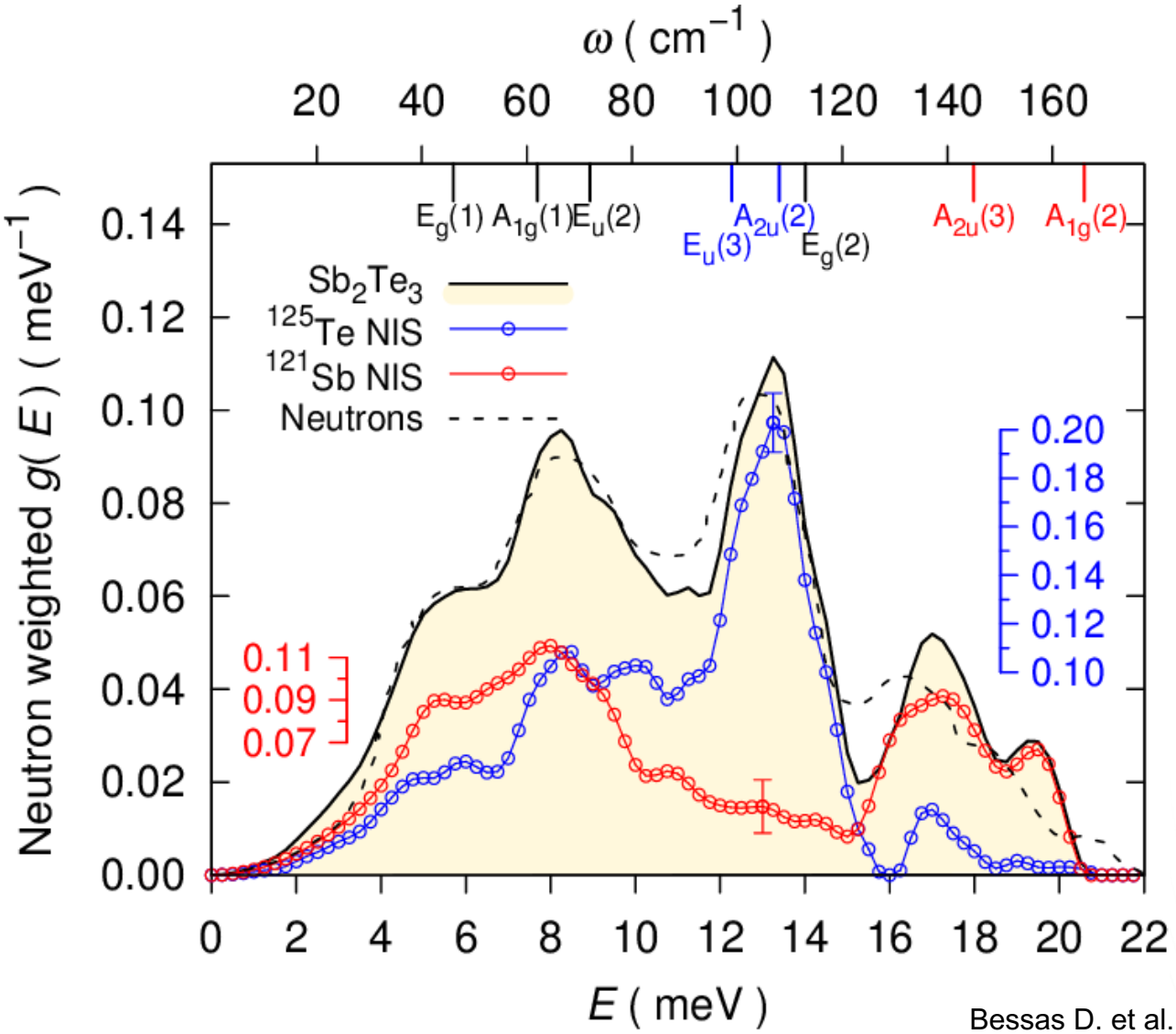


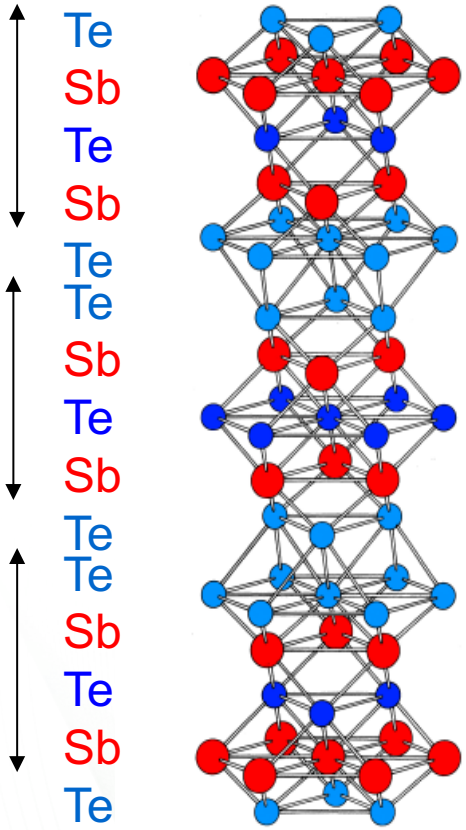
Rotational dynamics

ESRF, APS, SPring-8, PETRA III

Sergueev *et al.* ESRF Highlights (2002) pp. 61-62.

Sb_2Te_3 phonon spectoscopy



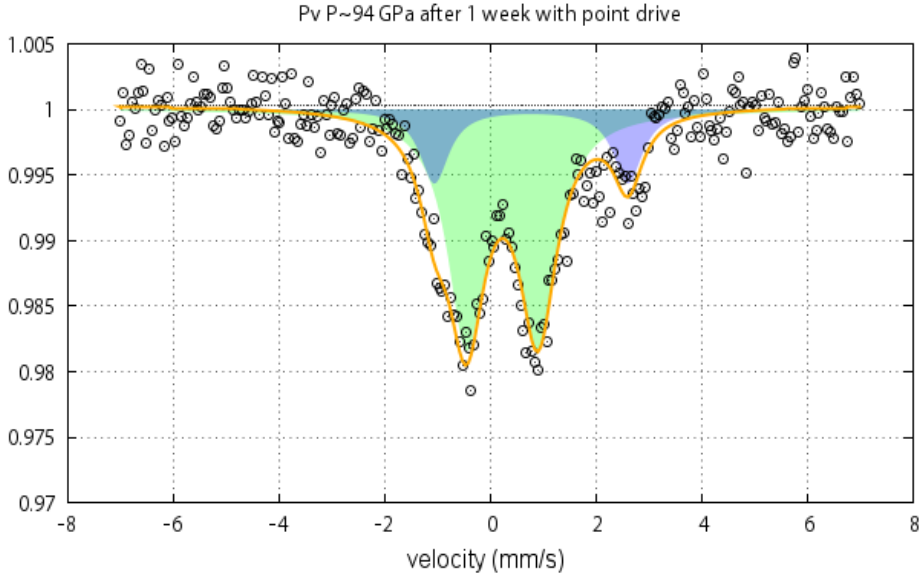


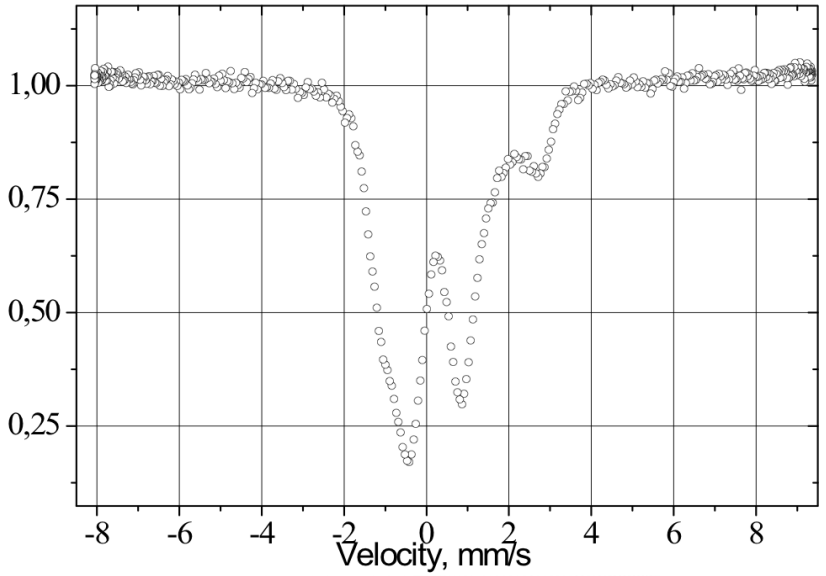
Bessas D. et al., *Phys. Rev. B* **86**, 224301 (2012).

Synchrotron Mössbauer Spectroscopy
Energy domain

Small samples → direct benefit from beam size

Perovskite at 94 GPa measured with a conventional source and with SMS
(same sample, same diamond anvil cell)





Measuring time ~ 10^4 min (one week) **Measuring time ~ 10 min**

SMS is three orders of magnitude faster

V. Potapkin, A.I. Chumakov, G.V. Smirnov , *et al*. (2012) J. Synchrotron Rad. (2012). 19, 559-569

- Historical perspective
- Spectral description and parameters
- Static interactions
- Time dependent interactions

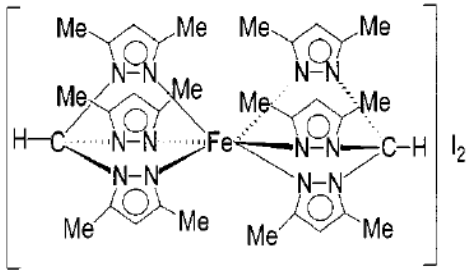
OAK RIDGE National Laboratory

Spin cross over in $\{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}I_2$

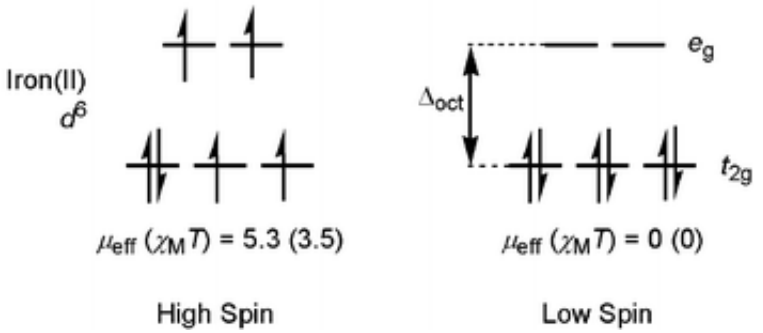
Reger, D. L. *et al., Eur. J. Inorg. Chem.* **2002,** 1190–1197 (2002).

Interest: memory, color change

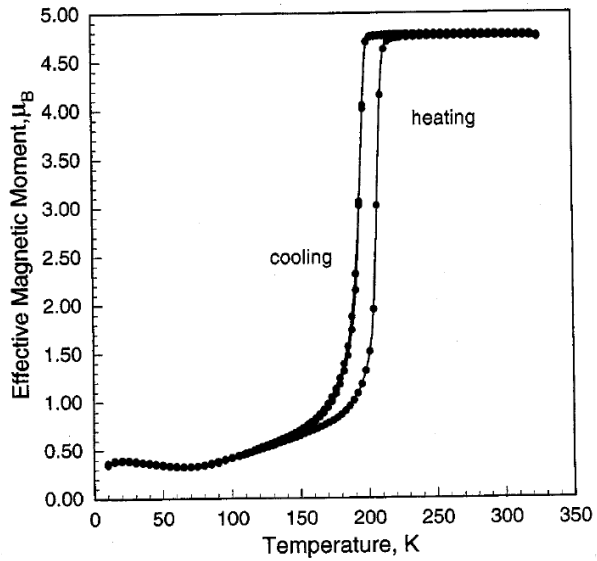
$$FeI_2 + 2HC(Me_2pz)_3 \xrightarrow{\text{acetone}} \{Fe[HC(3,5\text{-}Me_2pz)_3]_2\}I_2$$



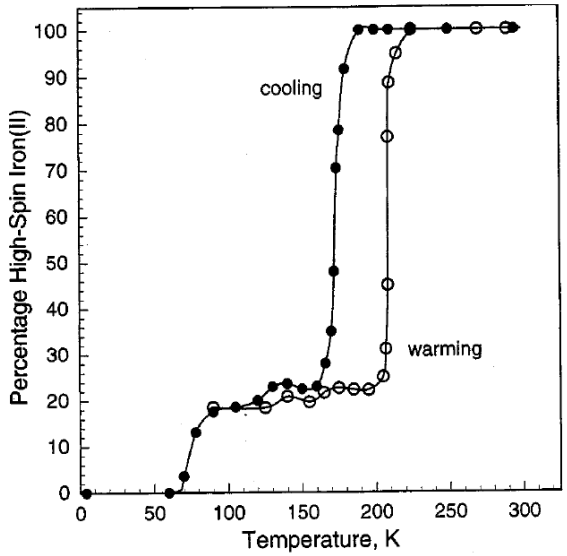
M. A. Halcrow, Chem. Soc. Rev., 37, 278-289 (2008)

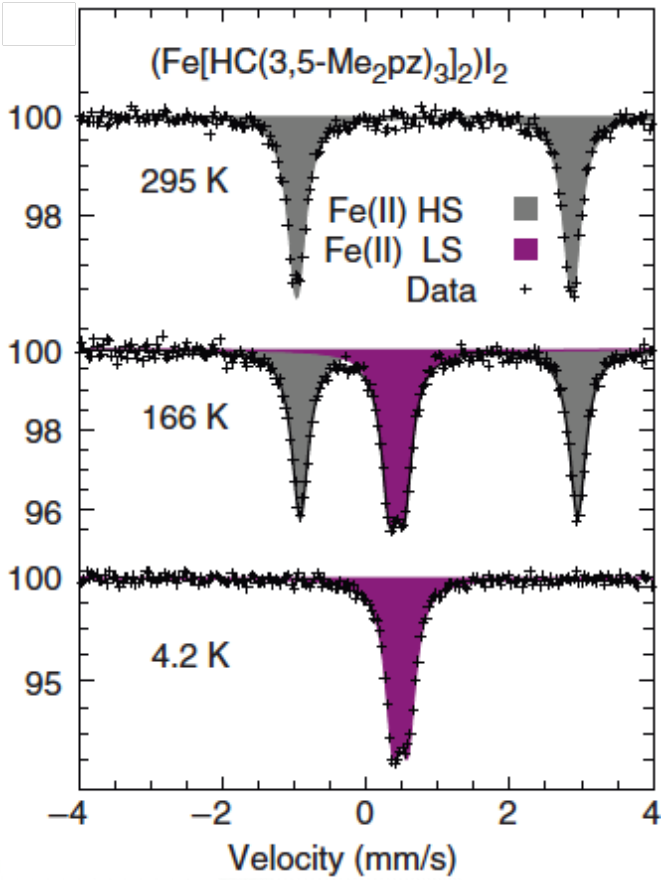


Magnetometry



Mössbauer



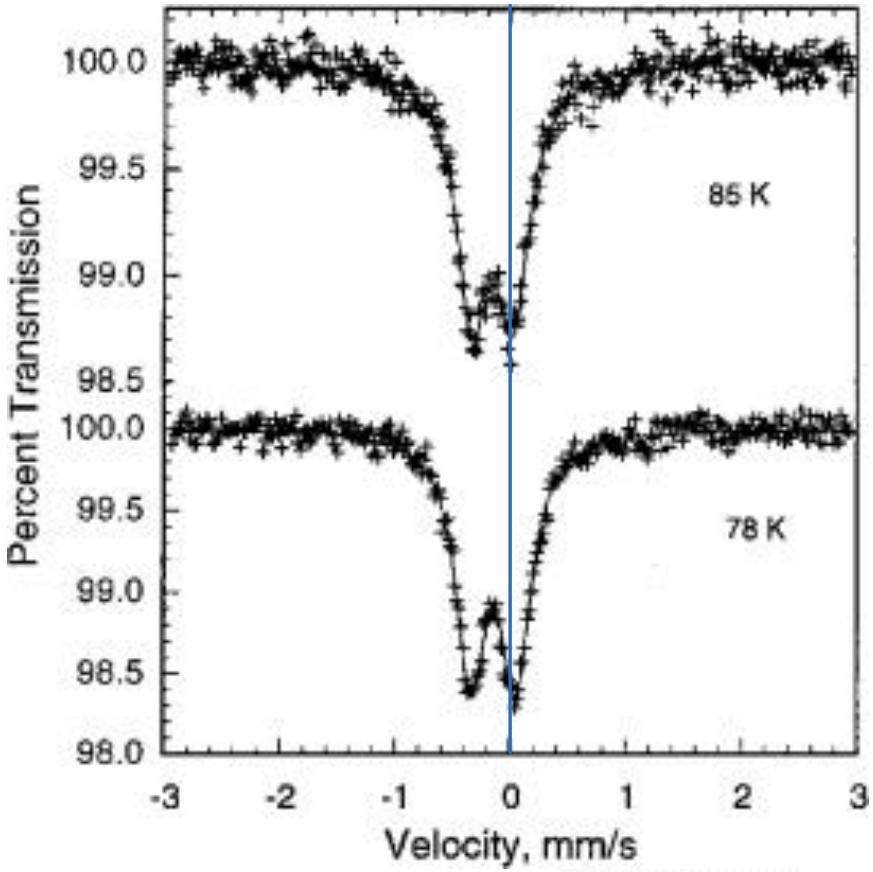


Oxidation states: Ba_2FeO_4 and Ba_3FeO_5

Interest: Oxidation agent and battery cathode

Delattre et al., Inorg. Chem. **41**, 2834-2838 (2002)

compound	T,K	δ, mm/s[a]	ΔE_Q, mm/s
Ba_2FeO_4	295	−0.244	0.33
	225	−0.185	0.34
	155	−0.169	0.35
	85	−0.152	0.36
Ba_3FeO_5	295	−0.225	0.35
	240	−0.204	0.34
	190	−0.199	0.37
	140	−0.168	0.40
	90	−0.150	0.39
	78	−0.142	0.39
		Fe(IV)	



-> magnetometry: μ_{eff} = 4.89 μ_B

Fe(IV) spin only moment: 4.9 μ_B

In contrast, isotructural Ba_3FeS_5 features Fe(III)

and the reduced iron yields a hole in the S^{2-} $3p^6$ band.

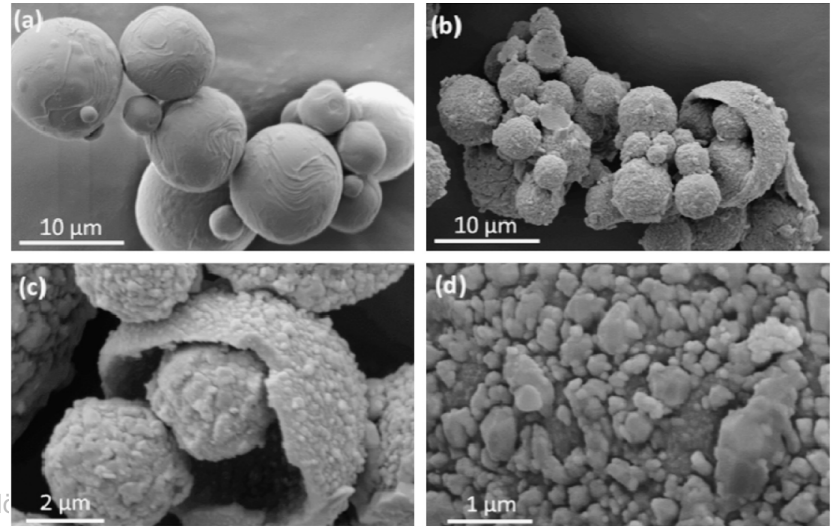
Screening synthesis conditions

NaFePO4F/carbon powder synthesis by spray drying
Application: cathode material for Li-, Na-ion batteries

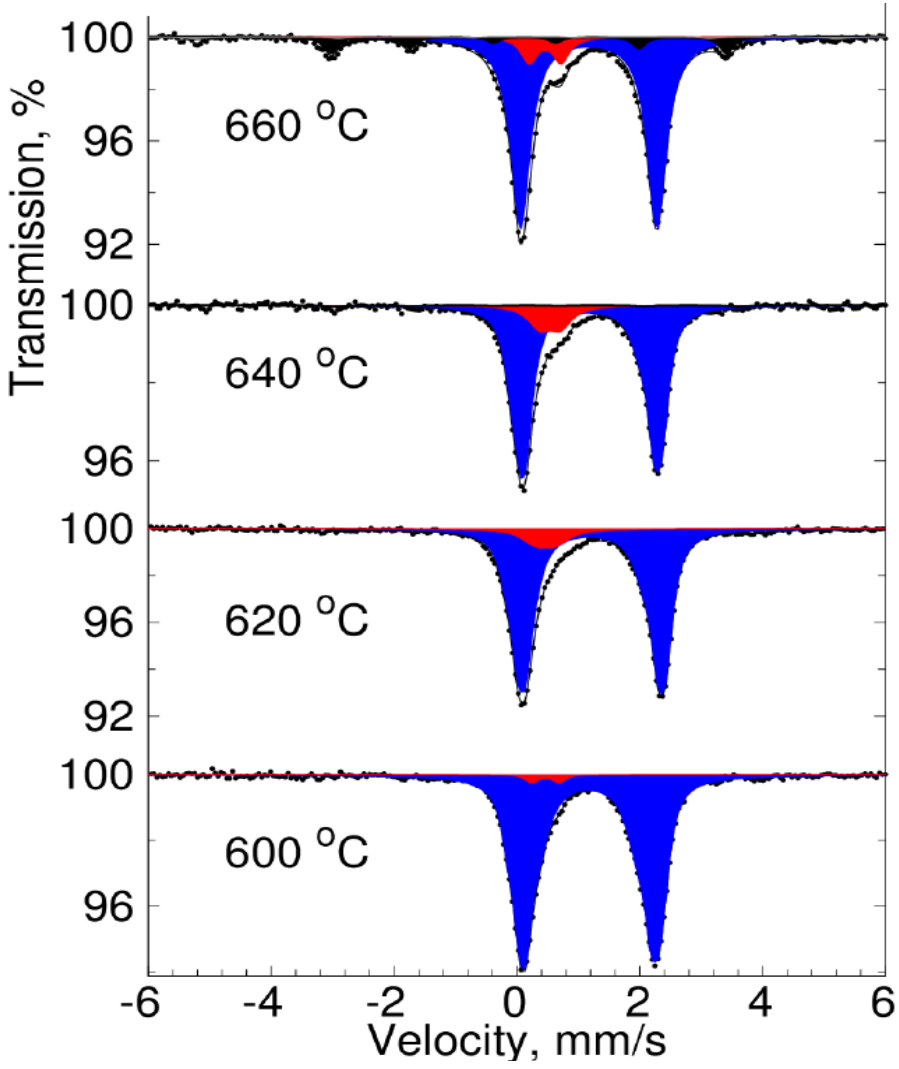
Synthesis parameters:
- **Fe (II) citrate + $NH_4H_2PO_4$, NaF and NaOH + deionized water**
- **final iron concentration of 0.1 mol/l**
- **solution spray-dried:**
  - **25 ml/min feed rate**
  - **140°C inlet temperature**
- **annealing at 600°C**

Optimised with "live" Mössbauer spectral feedback for Fe(II)/Fe(III) content

Before annealing After annealing at 600 °C



Annealing sequence



Brisbois et al., *Materials Letters* **130** (2014), 263.

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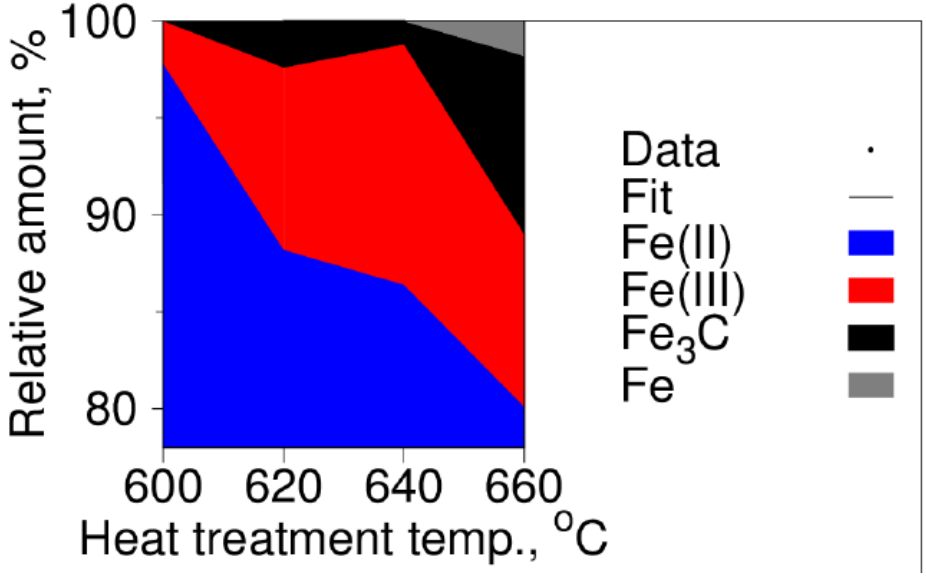
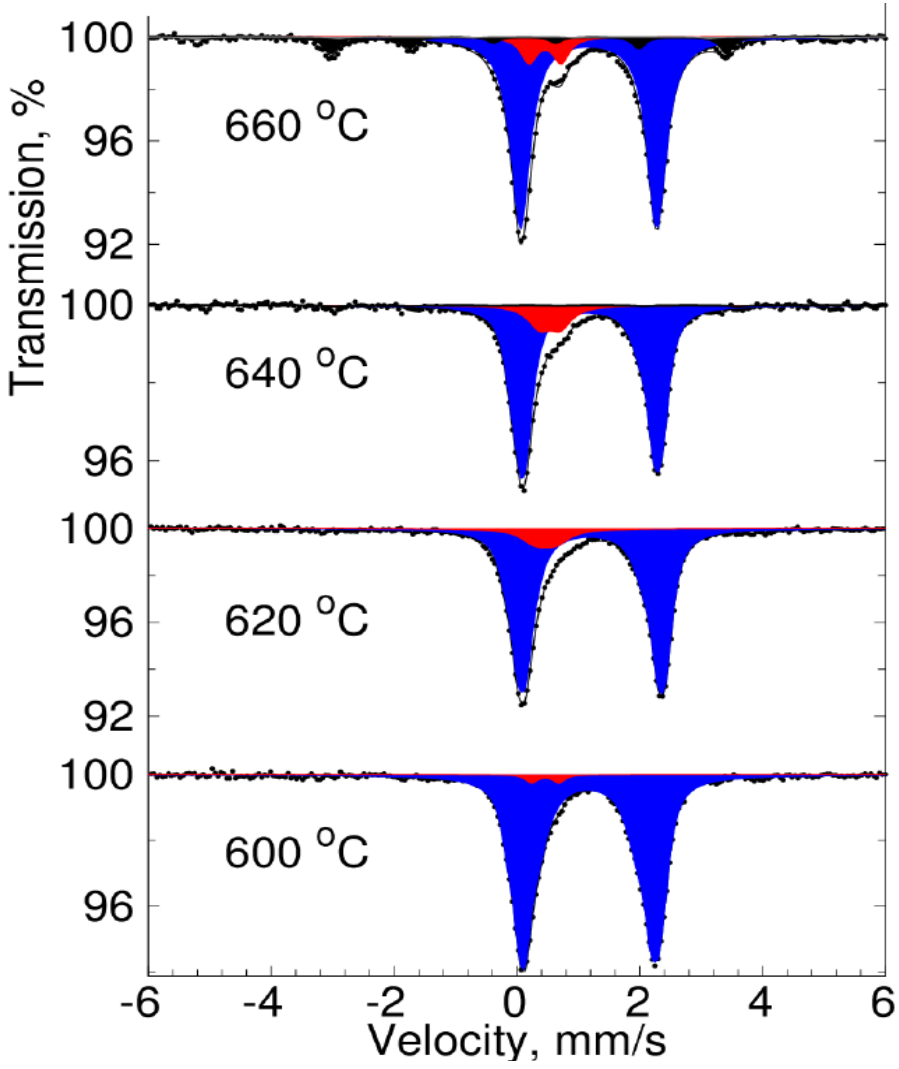
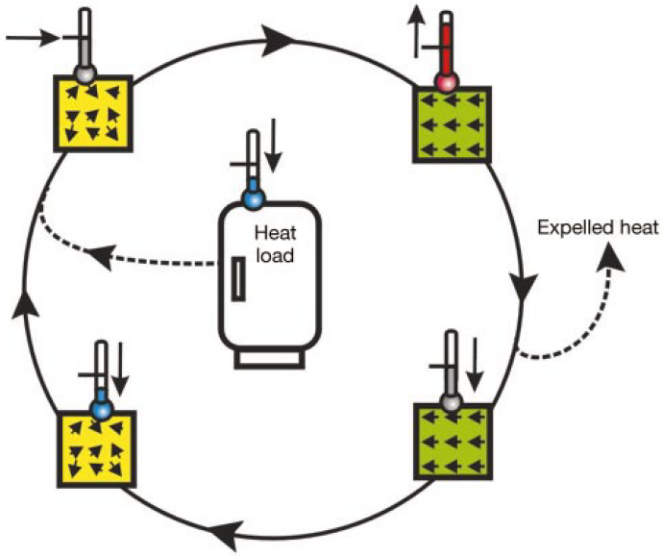


Annealing sequence



Brisbois et al., *Materials Letters* **130** (2014), 263.

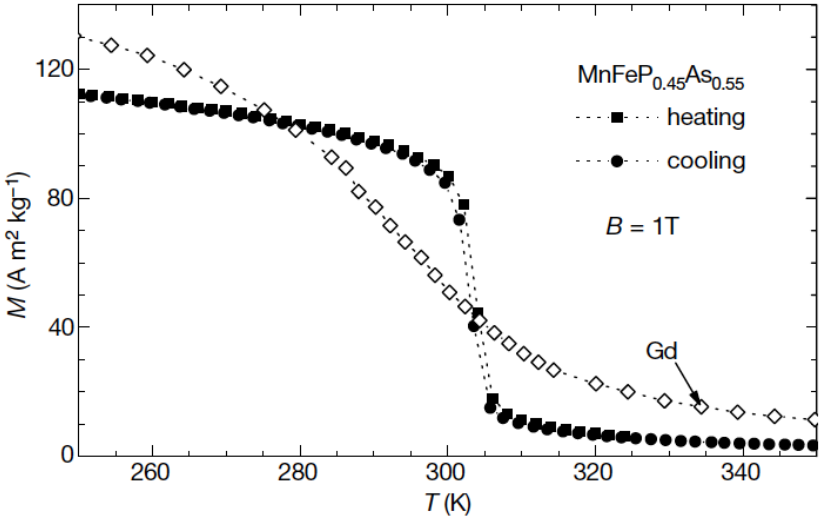
Magnetocaloric $FeMnP_{1-x}As_x$



The application of a magnetic field aligns the magnetic moments, reduces the magnetic entropy and increases the (lattice) temperature.

The removal of the magnetic field yields a randomization of the moments, increases the spin entropy and decreases the (lattice) temperature.

The sharp magnetic transition in $FeMnP_{1-x}As_x$ yields a cooling efficiency of ~20 J/K/kg similar to Gd for operation around ~300 K.



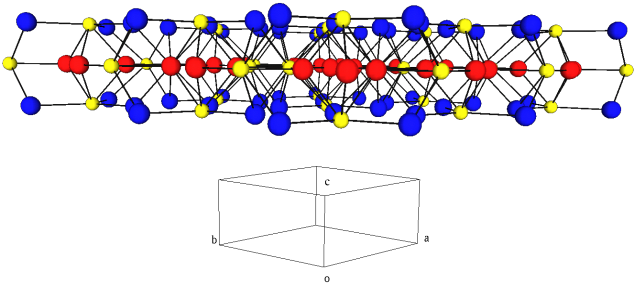
Jan. 2015: product presented CES Las Vegas

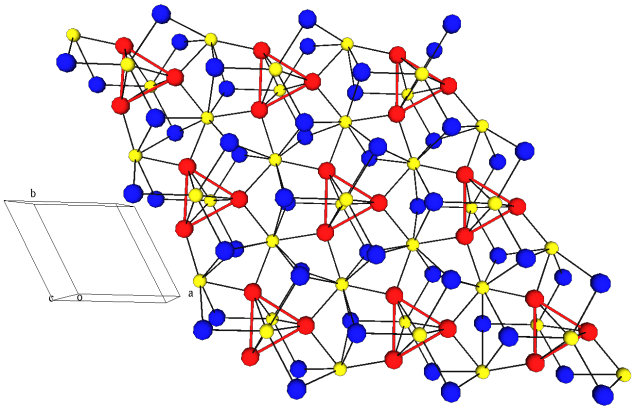
Material: FeMn(P,Si)

Tegus O., Brück E., Buschow K. H. J., and de Boer F. R., Nature **415**, 150 (2002).

$FeMnP_{1-x}As_x$ structure

Iron and manganese layers perpendicular *c*
Iron has four P or As near-neighbors.





Triangular iron groups in the *ab* plane.

The 5 % component corresponds to iron that occupies the manganese site.

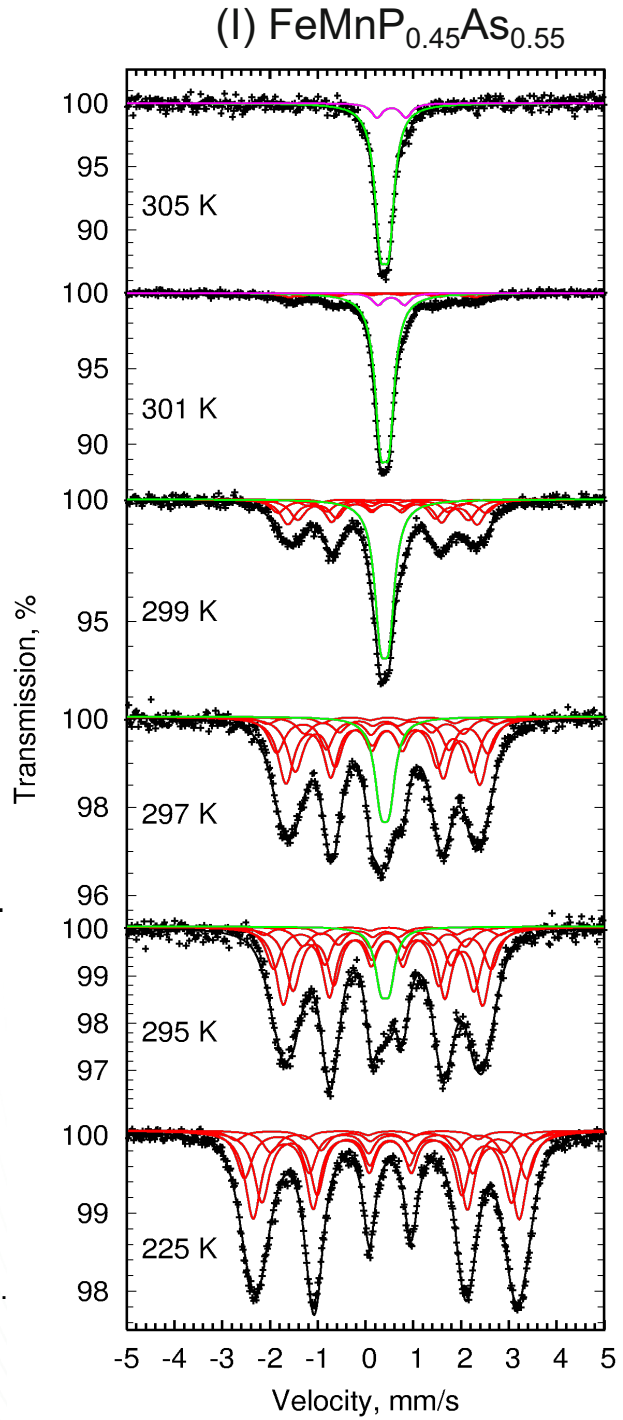
The paramagnetic and ferromagnetic states coexist over a range of ~10 K.

The hyperfine field at 301 K is only slightly smaller than at 225 K.

The magnetic transition is first-order in agreement with the magnetization.

The ferromagnetic subspectra correspond to the binomial P and As near-neighbor distribution components.

$$P(n) = C_4^n x^n (1-x)^{4-n}$$



Malaman *et al.*, J. Phys.: Cond. Matter **8**, 8653 (1996).
Hermann et al., Phys Rev B **70**, 214425 **(**2004**)**

Incommensurate magnetism

The ferromagnetic subspectra are constrained, except relative area.

The antiferromagnetic subspectra are fitted by taking into account

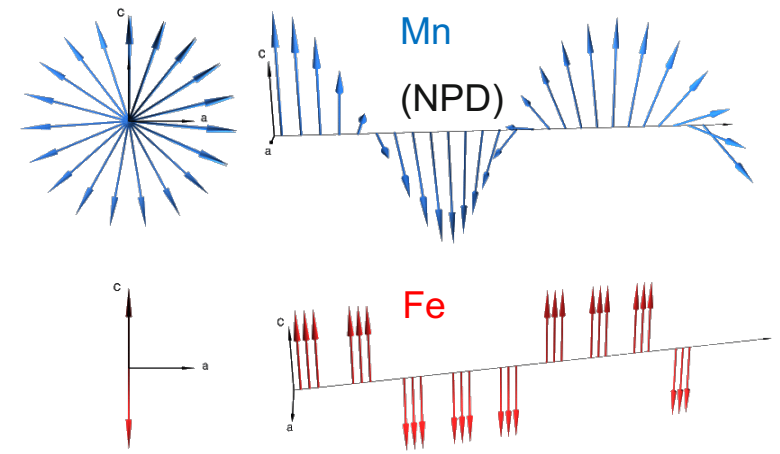
the binomial distribution, (poor fits ...)
the incommensurate antiferromagnetic structure, (poor fits ...)

$$H_{AF} = C\mu \sin\theta,$$

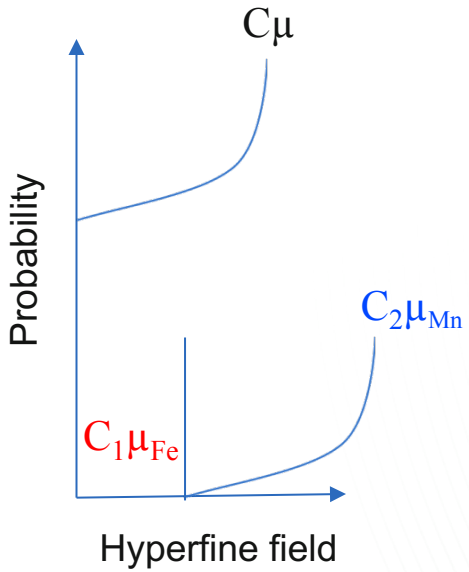
and the contribution from the **two** magnetic sub-lattices. (good fits)

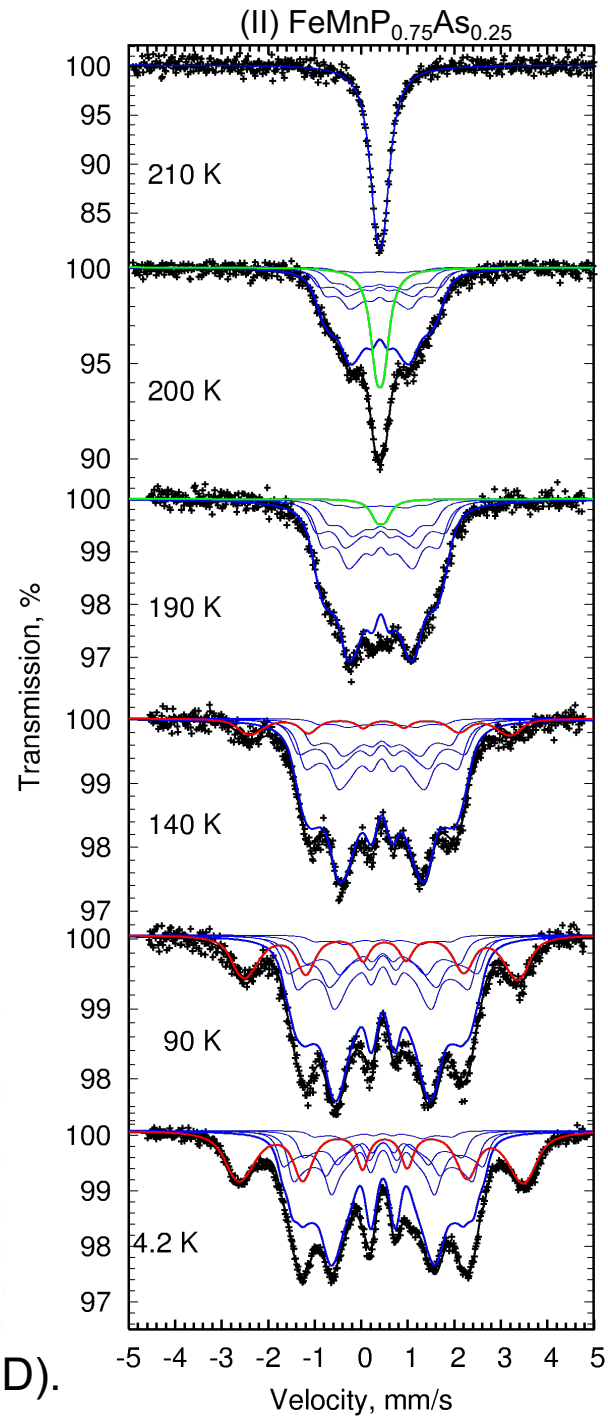
$$H_{AF} = C_1\mu_{Fe} + C_2\mu_{Mn} \sin\theta$$

The last addition introduces a single free parameter.



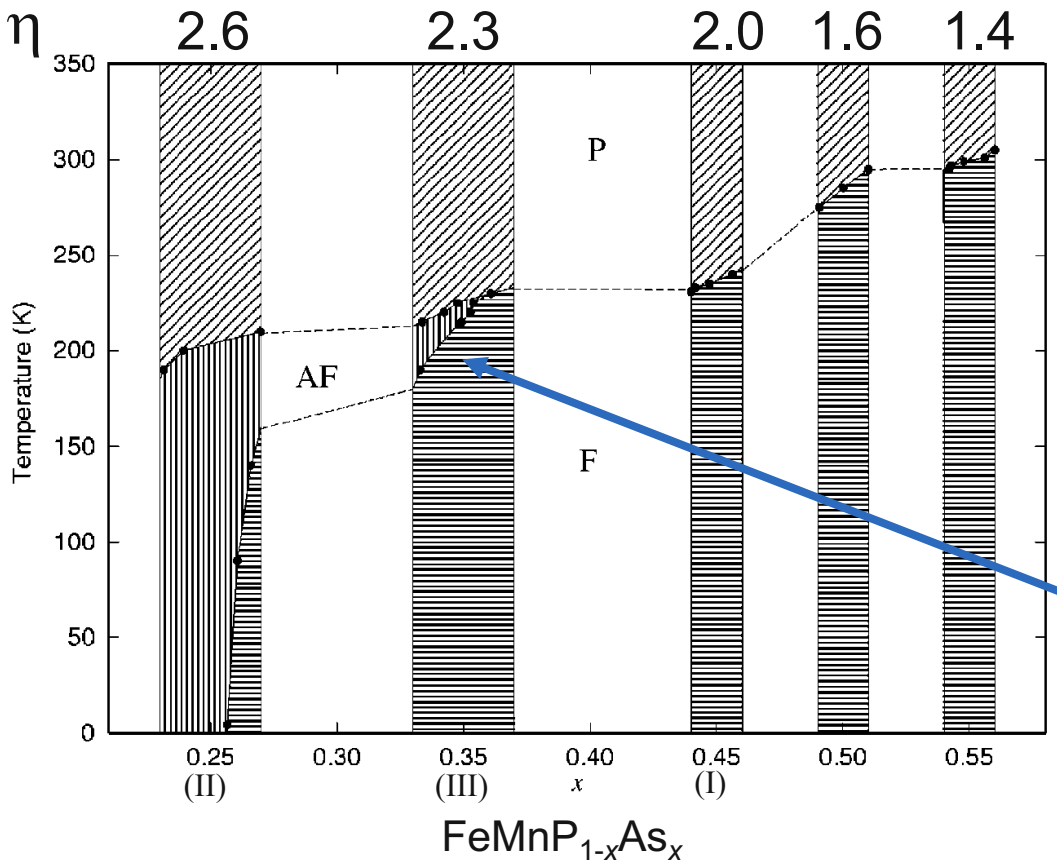
Hermann et al., Phys Rev B **70**, 214425 **(**2004**)**

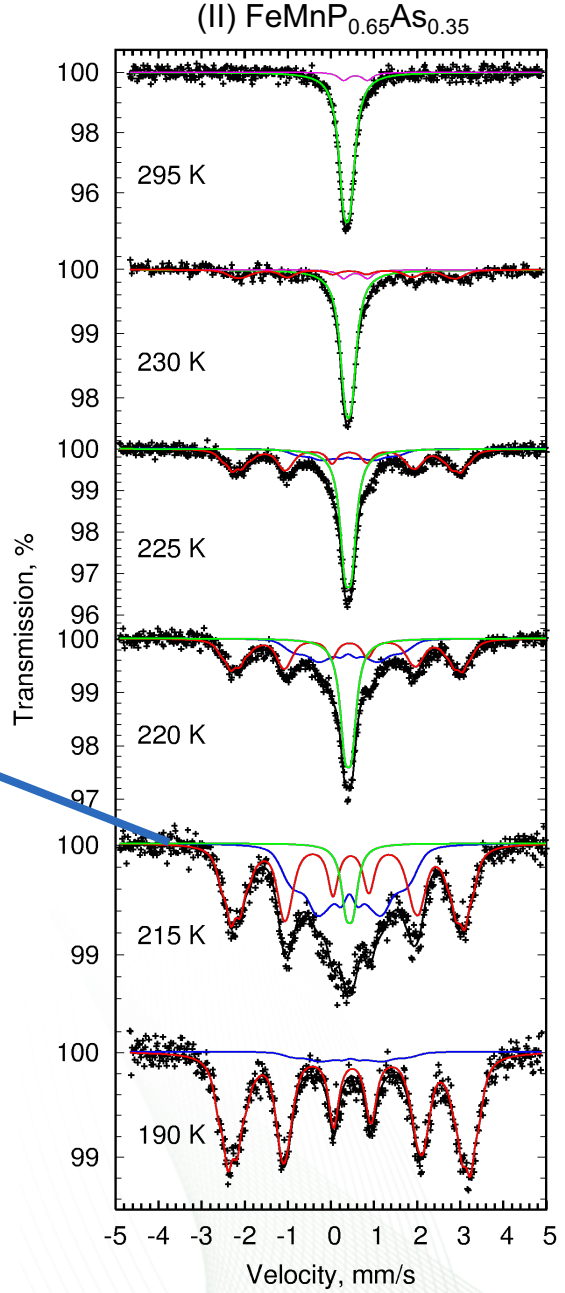




$\theta = 2\pi.x_M/a_M$, position of the nucleus/magnetic lattice constant (1D).

Magnetic phase diagram





Magnetic triple point: the ferromagnetic, antiferromagnetic, and paramagnetic phases coexist at T ~220 K.

Spectra for x = 0.55, 0.50, 0.45, 0.35, and 0.25 can be summarized in a phase diagram by assuming a compositional inhomogeneity, Δx.

The order of the transition, $\eta > 1$, indicating first order character. (Bean and Rodbell model for magnetostriction exchange)

Carbodiimides – new pseudooxides

M^{2+} $[^{-}N=C=N^{-}]$

- 3D non-oxidic extended frameworks, new class of materials
- -N=C=N- (-2) is among the shortest and simplest bridging anions
- linear geometry is at variance with -O- bridging
- how is magnetic exchange between transition metals or rare-earth affected?

Historically: main use as calcium cyanamide as fertilizer.

In contact with water: $CaNCN + 3\ H_2O \rightarrow 2\ NH_3 + CaCO_3$

Also used in steelmaking → introduces nitrogen

Magnetic properties

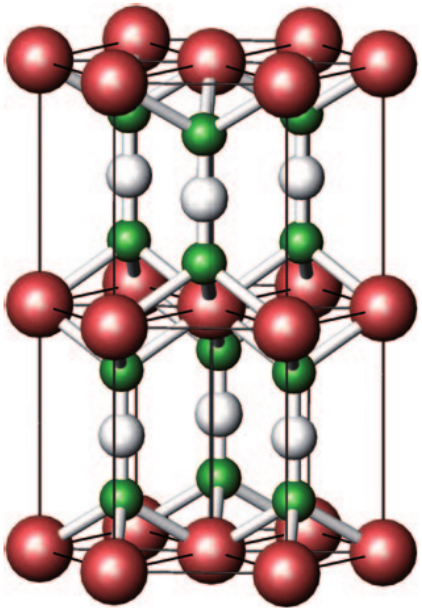
→MnNCN, CoNCN, NiNCN and CuNCN are „nitrogen based pseudo-oxides“ [4]
MnO, CoO, NiO, and CuO.

→ Gapped insulators: MnNCN is green, FeNCN dark red, CoNCN orange-brown, NiNCN light-brown, close to *M*O compounds

→ [NiAs] and not [NaCl] type structure, for FeNCN, close to delafossite CuFeO2.

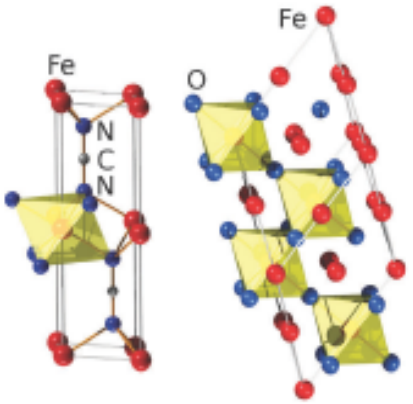
→ Néel temperatures

	- O^{-2}	- NCN^{-2}
Mn^{+2}	119 K [1]	30 K [2]
Fe^{+2}	198 K [3]	350 K [4]
Co^{+2}	289 K [1]	255 K [4]
Ni^{+2}	524 K [1]	360 K [4]

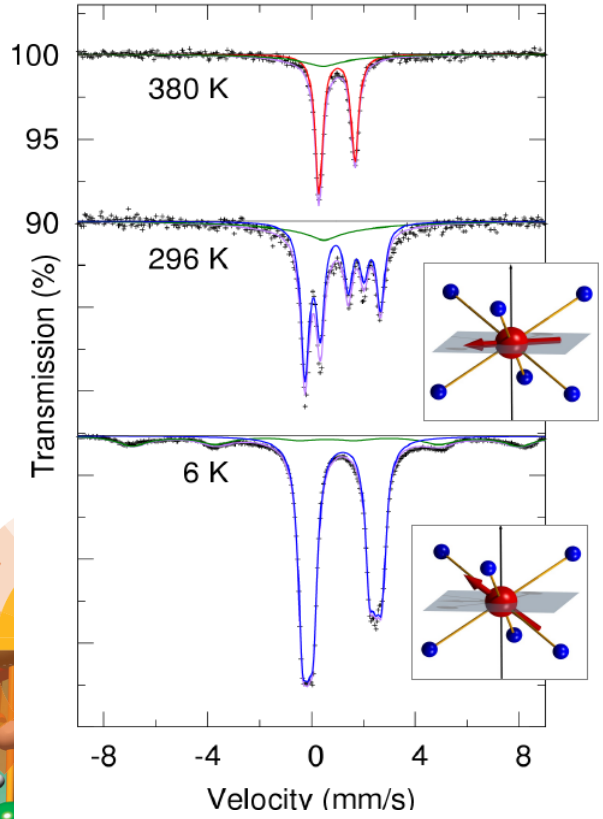


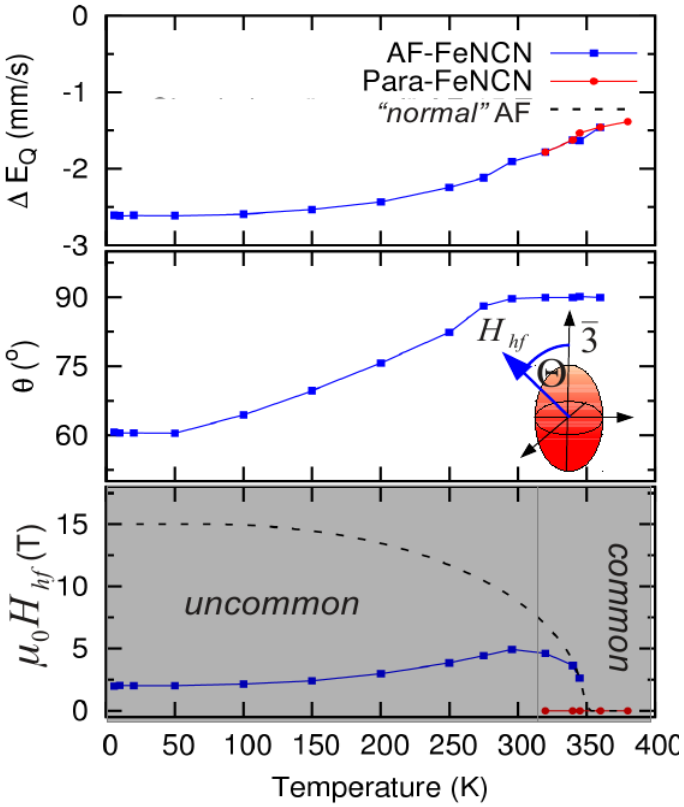
[1] G. Srinivasan *et al.*, Phys. Rev. B **28**, 6542 (1983).
[2] X. Liu *et al.*, Inorg. Chem. **44**, 3001−3003 (2005).
[3] G. Kugel *et al.*, Phys. Rev. B **16**, 378–385, (1977).
[4] X. Liu *et al.*, Chem. Eur. J. **15**, 1558 – 1561 (2009).
[5] M. Krott *et al.*, Inorg. Chem. **46**, 2204−2207 (2007).

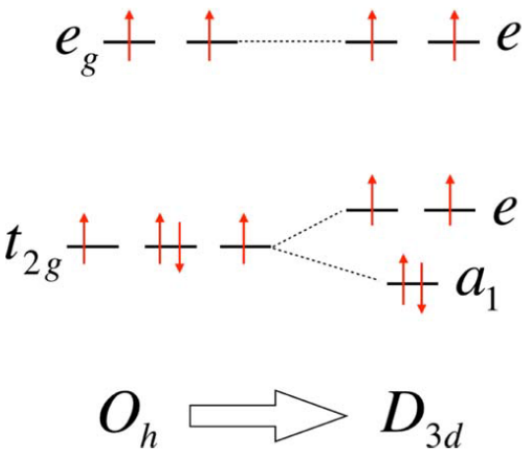
Mössbauer spectra of FeNCN



M. Herlitschke, *et al.*
New J. Chem., 2014, 38, 4670







Thermal activation:

change of ΔE_Q

Orbital moment arises

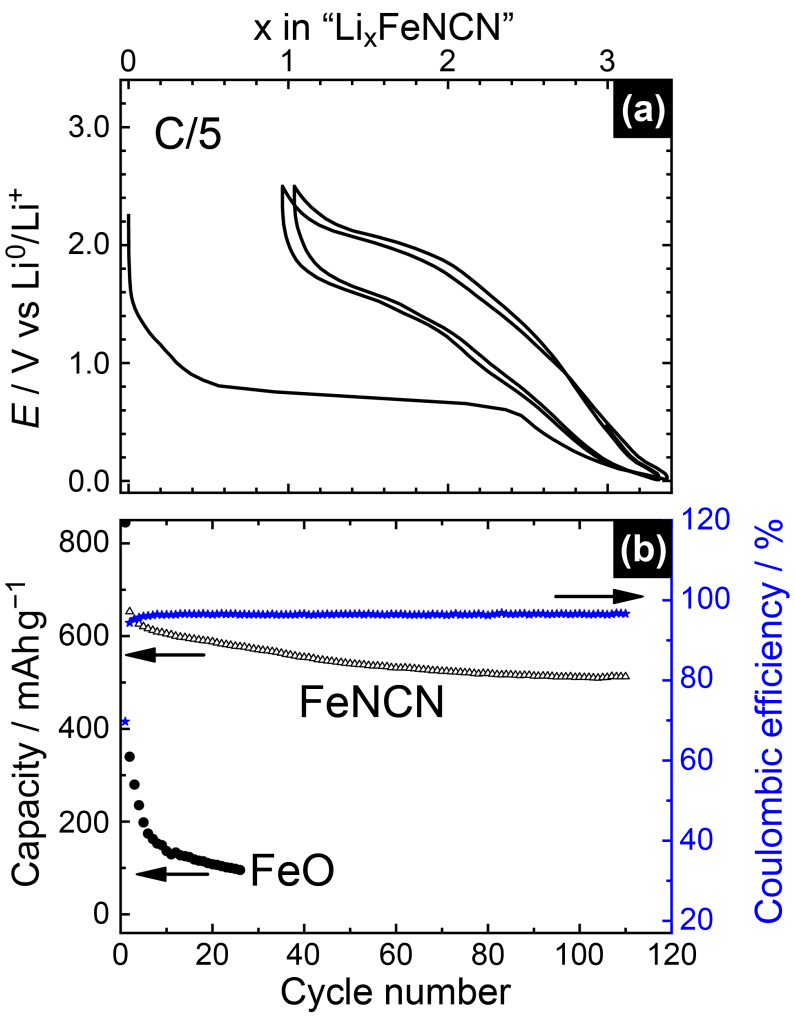
(degenerated by excitations)

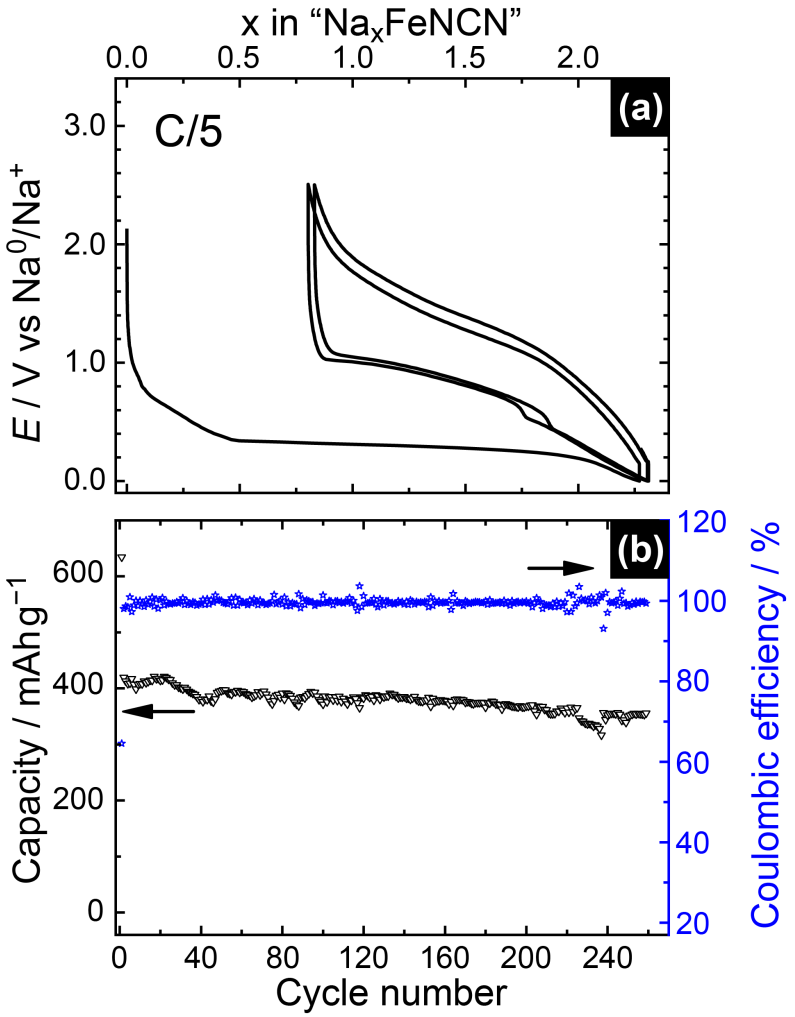
Dipole interaction changes

Tchougréeff *et al.*, Int. J. of Quantum Chem. **116**, 282–294 (2016)

“Transition-metal carbodiimides as new molecular negative electrode materials for Li- and Na-ion batteries with excellent cycling properties”

M. T. Sougrati et al., Angewandte Chemie, accepted Feb. 2016





Analogous reactions for MnNCN, ZnNCN and $Cr_2(NCN)_3$

“Transition-metal carbodiimides as new molecular negative electrode materials for Li- and Na-ion batteries with excellent cycling properties”

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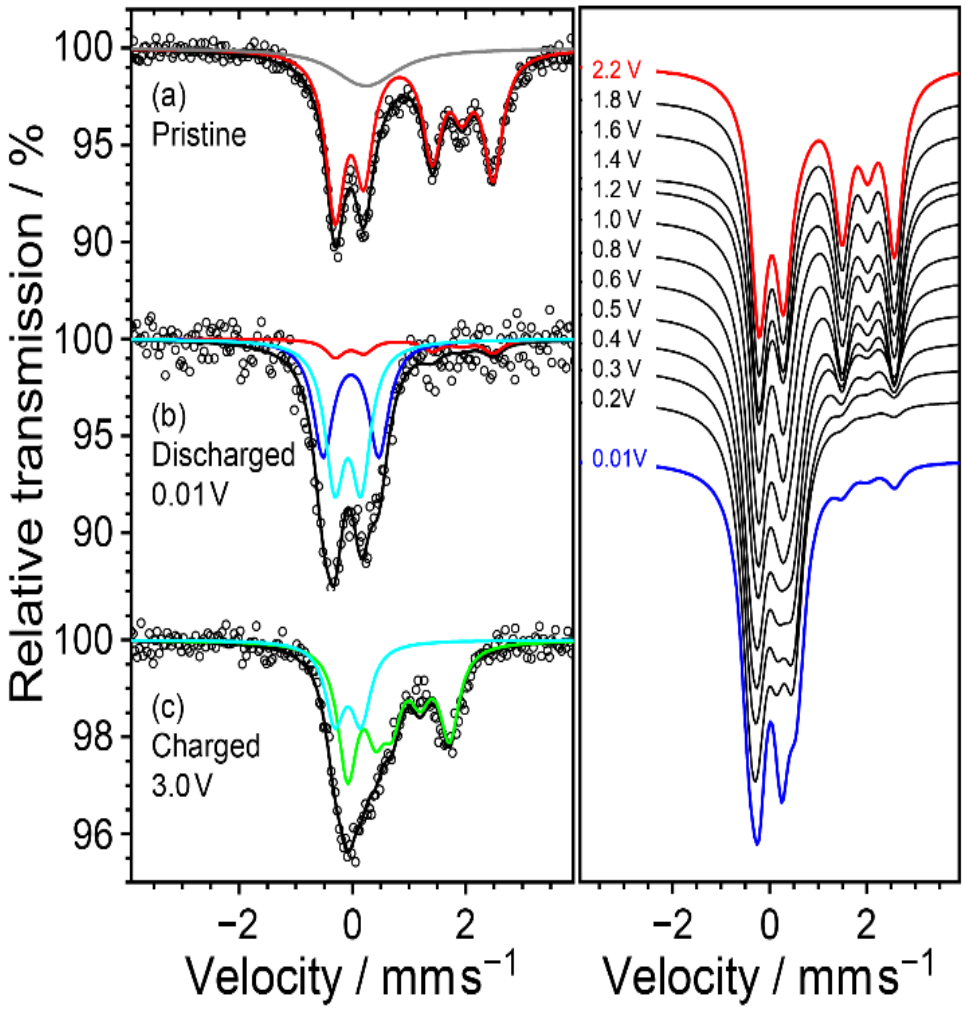


$$FeNCN_{(s)} + 2\,Li_{(s)} \rightleftharpoons Fe_{(s)} + Li_2NCN_{(s)}$$

Analogous reactions for MnNCN, ZnNCN and $Cr_2(NCN)_3$

Electrochemical cell for *Operando* XRD and Mössbauer studies developed by Leriche et al. (*J. Electrochem. Soc. Vol. 157 (2010)*)

M. T. Sougrati, A. Darwiche, L. Monconduit, L. Stievano, R. P. Hermann, A. Mahmoud, M. Herlitschke, R. Dronskowski, X. Liu, *Metal Carbodiimides and Metal Cyanamides as New Active Electrode Materials*, EP15305888 (2015), European Patent pending.

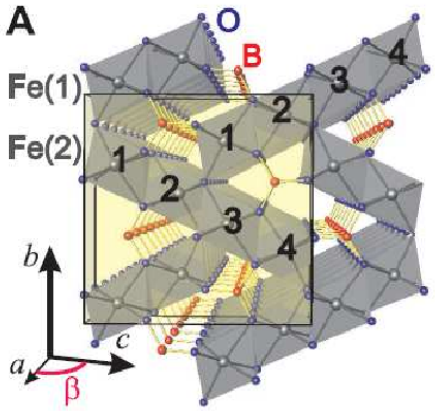
- Historical perspective
- Spectral description and parameters
- Static interactions
- Time dependent interactions

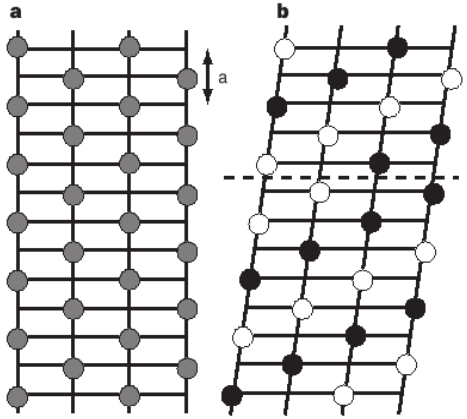
Charge order / electron hopping in Fe_2OBO_3

Evidence: Mössbauer spectroscopy, change in resistivity

Proposed structure [Attfield *et al.*, Nature **396**, 655 (1998)]

(from powder data)

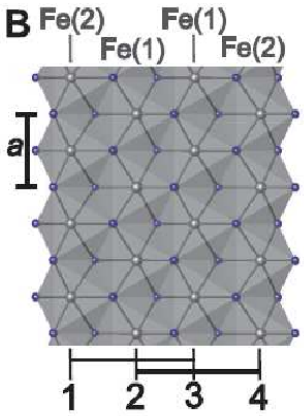


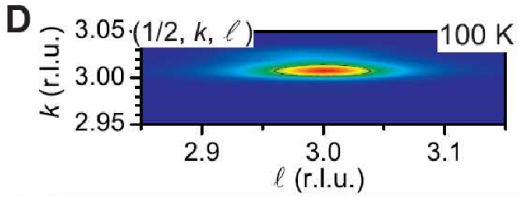


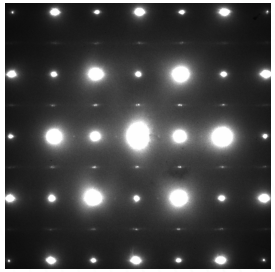
Single crystal growth [Angst, 2005; ORNL]

Single crystal diffraction: detailled structure

Synchrotron radiation and electron scattering: CO peaks!

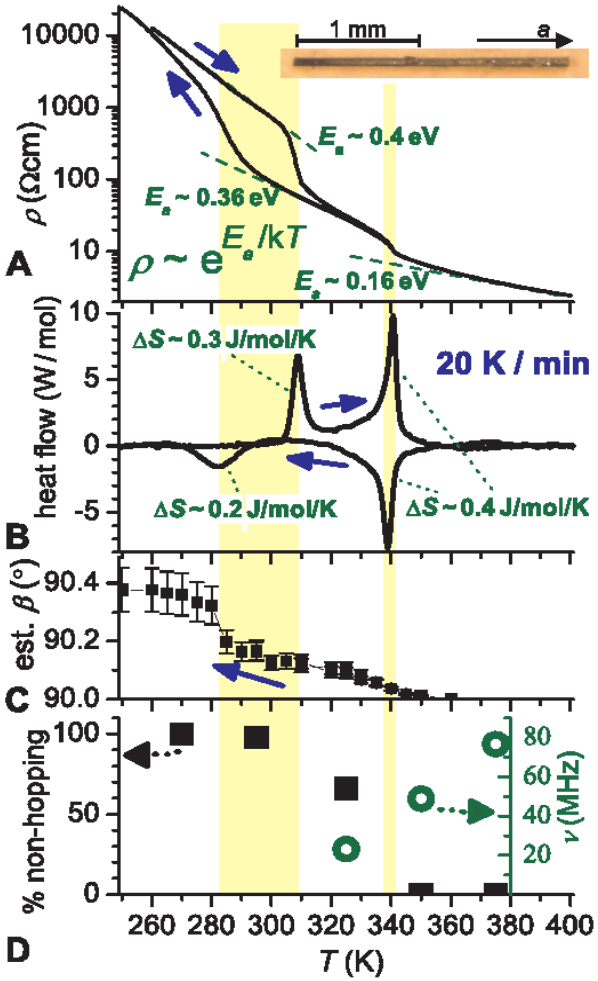


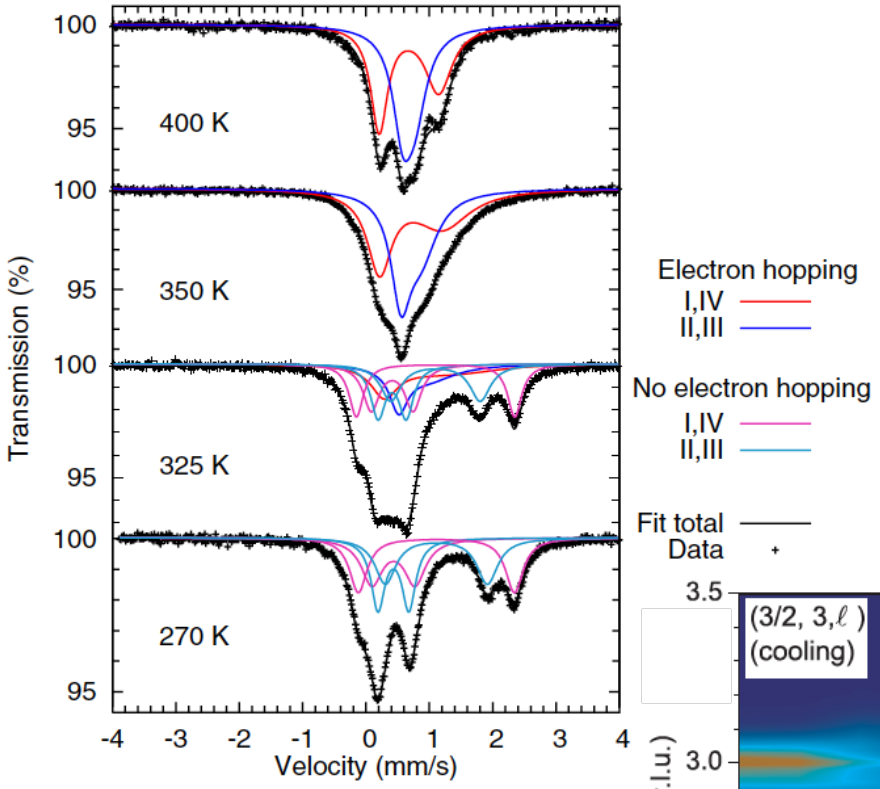


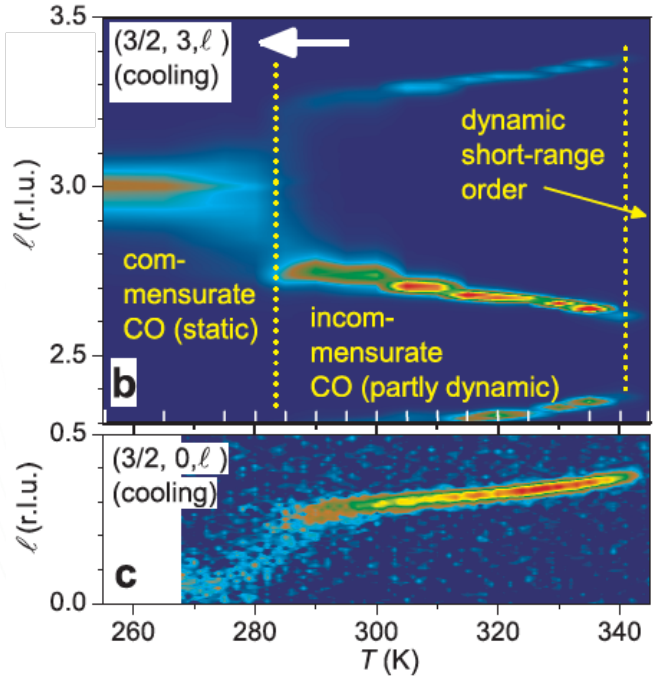


Angst, M. *et al.*, *Phys. Rev. Lett.* **99,** 256402 (2007).
Angst, M. *et al., Phys. Rev. Lett.* **99,** 086403 (2007).

Charge order / electron hopping in Fe_2OBO_3







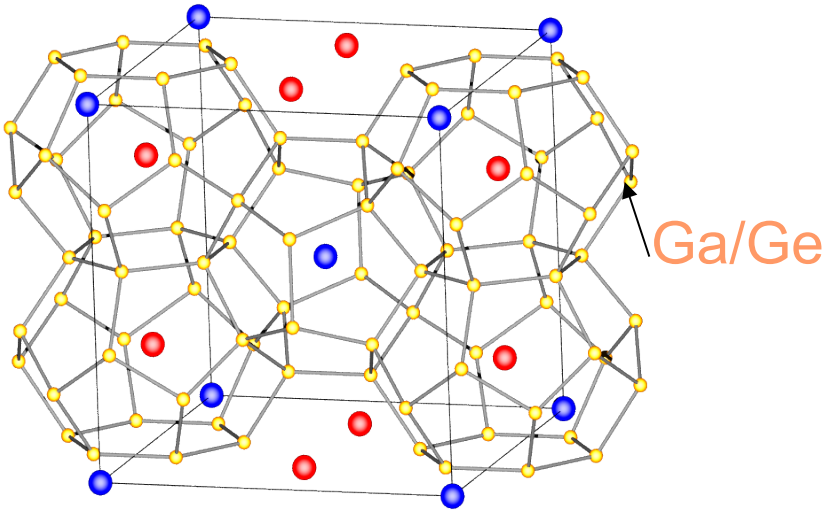
Intermediate phase:300-340 K,

incommensurate charge order

Angst, M. *et al.*, *Phys. Rev. Lett.* **99,** 256402 (2007).
Angst, M. *et al., Phys. Rev. Lett.* **99,** 086403 (2007).

Guest dynamics in AGa$_{16}$Ge$_{30}$ clathrates

2a A(I) and 6d A(II) sites are occupied by either Ba, Eu, or Sr.

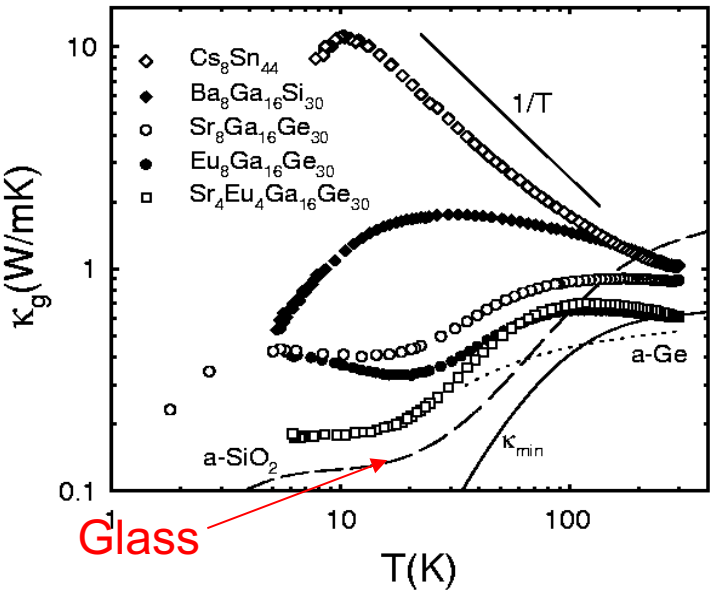


The structure consists of stacked small cages with A(I) and large cages with A(II) on/near the center.

Filled clathrate are interesting as

- potential thermoelectric materials,
- model systems for caged atoms.

Low, anomalous thermal transport.



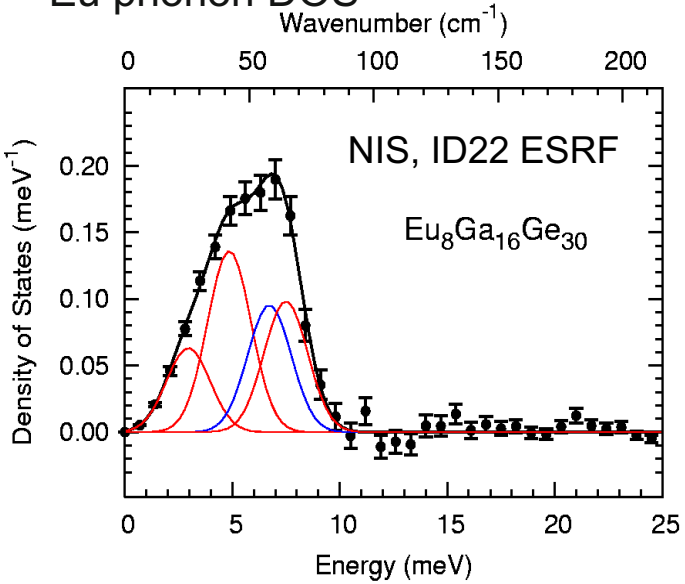
Cohn *et al.*, *PRL* **82**, 779 (1999)

OAK RIDGE National Laboratory

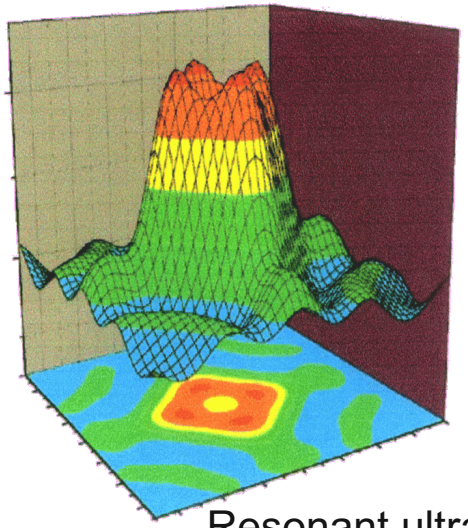
Potential landscape

Sales B. C., Chakoumakos B. C., Jin R., Thompson J. R., and Mandrus D., *Phys. Rev. B* **63**, 245113 (2001).

^{151}Eu phonon DOS

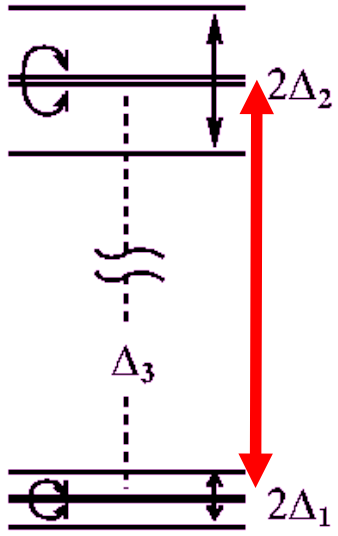


Hermann et al., *Phys. Rev. B* **72**, 174301 (2005)



Resonant ultrasound spectroscopy response

Static or dynamic disorder in the ground state?

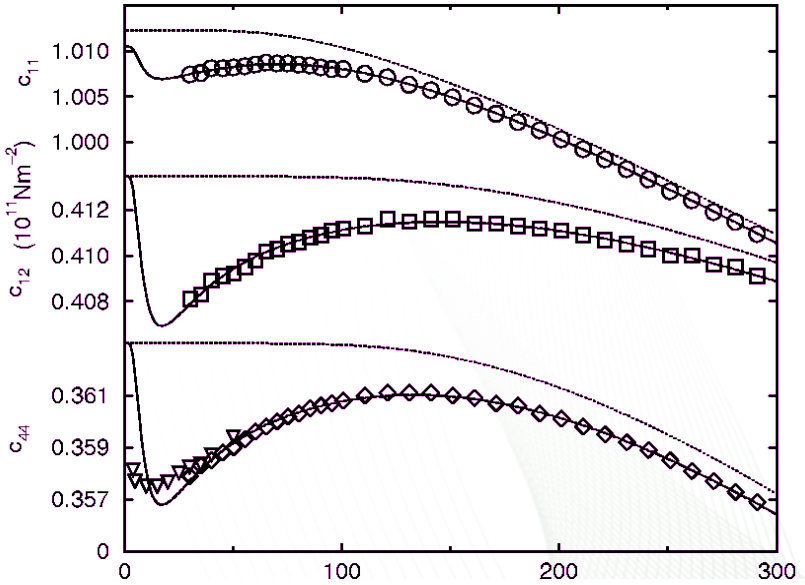


~ 3 meV

50 mK

~ 4.3 μeV

~ 1 GHz



Zerec I., Keppens V., McGuire M. A., Mandrus D., Sales B. C., and Thalmeier P., Phys. Rev. Lett. 92, 185502 (2004).

Mössbauer spectra

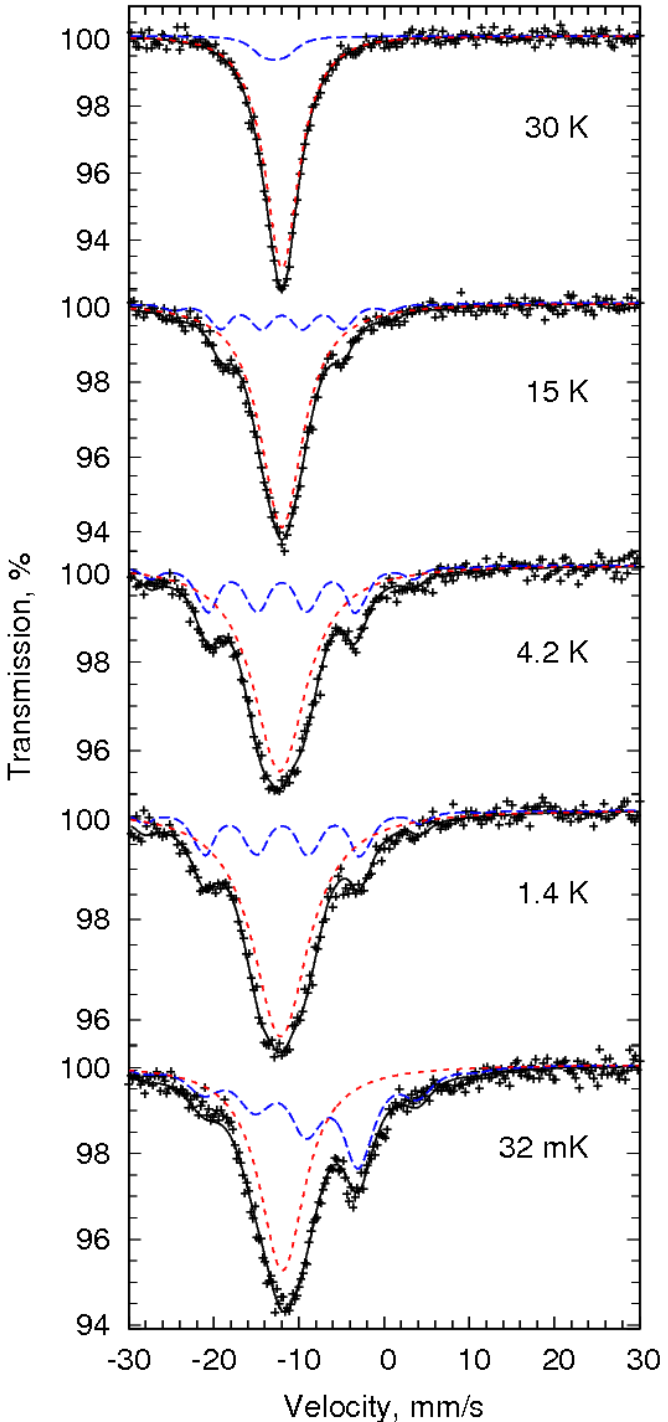
Eu(I) and Eu(II) Eu2+ spectral components overlap.

Eu(I) exhibits magnetic splitting with T_c ~30 K.

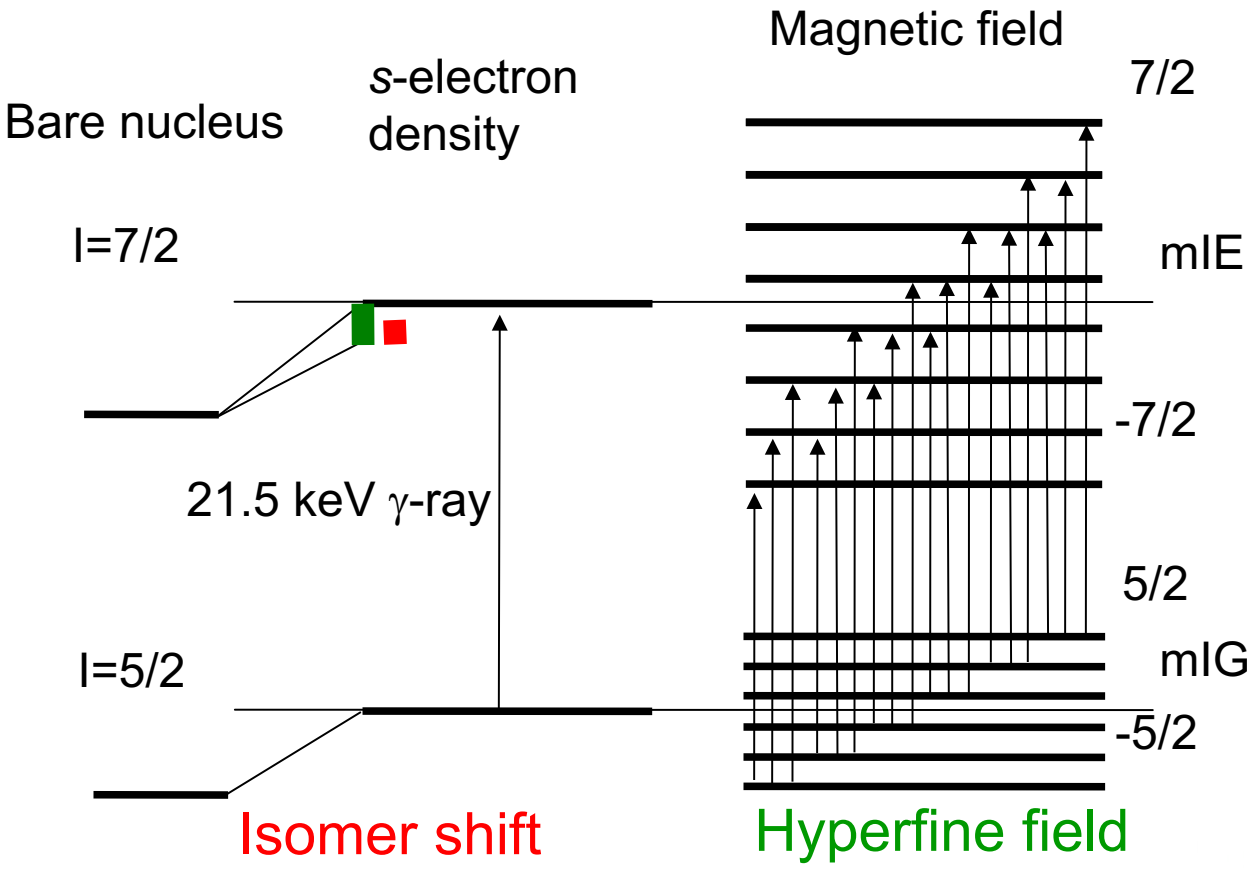
Eu(II) exhibits no magnetic splitting even at 32 mK.

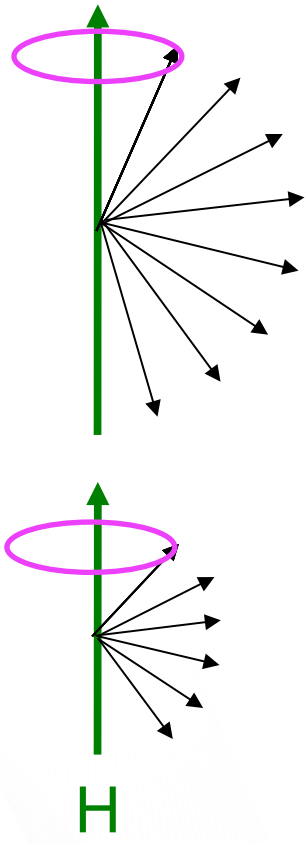
Neutron diffraction and magnetization measurements indicate 7 μ_B moments for **all** Eu.

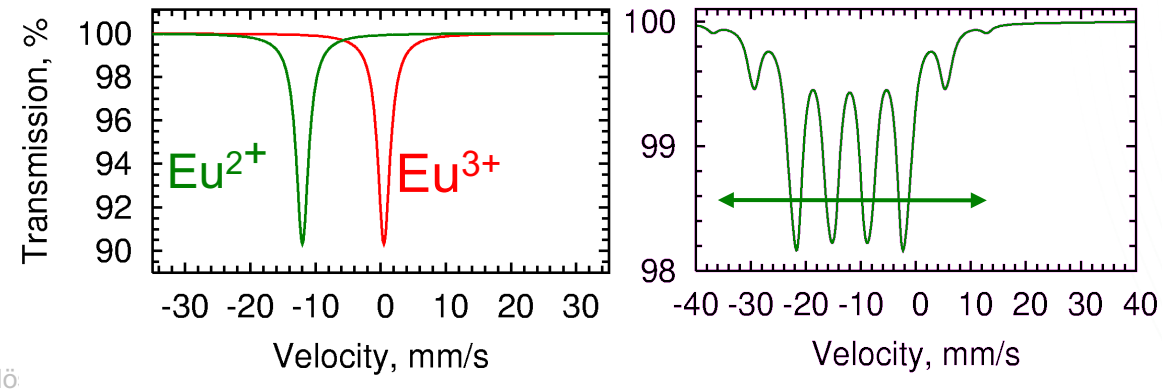
Hypothesis: we observe jump diffusion or tunneling induced magnetic relaxation.



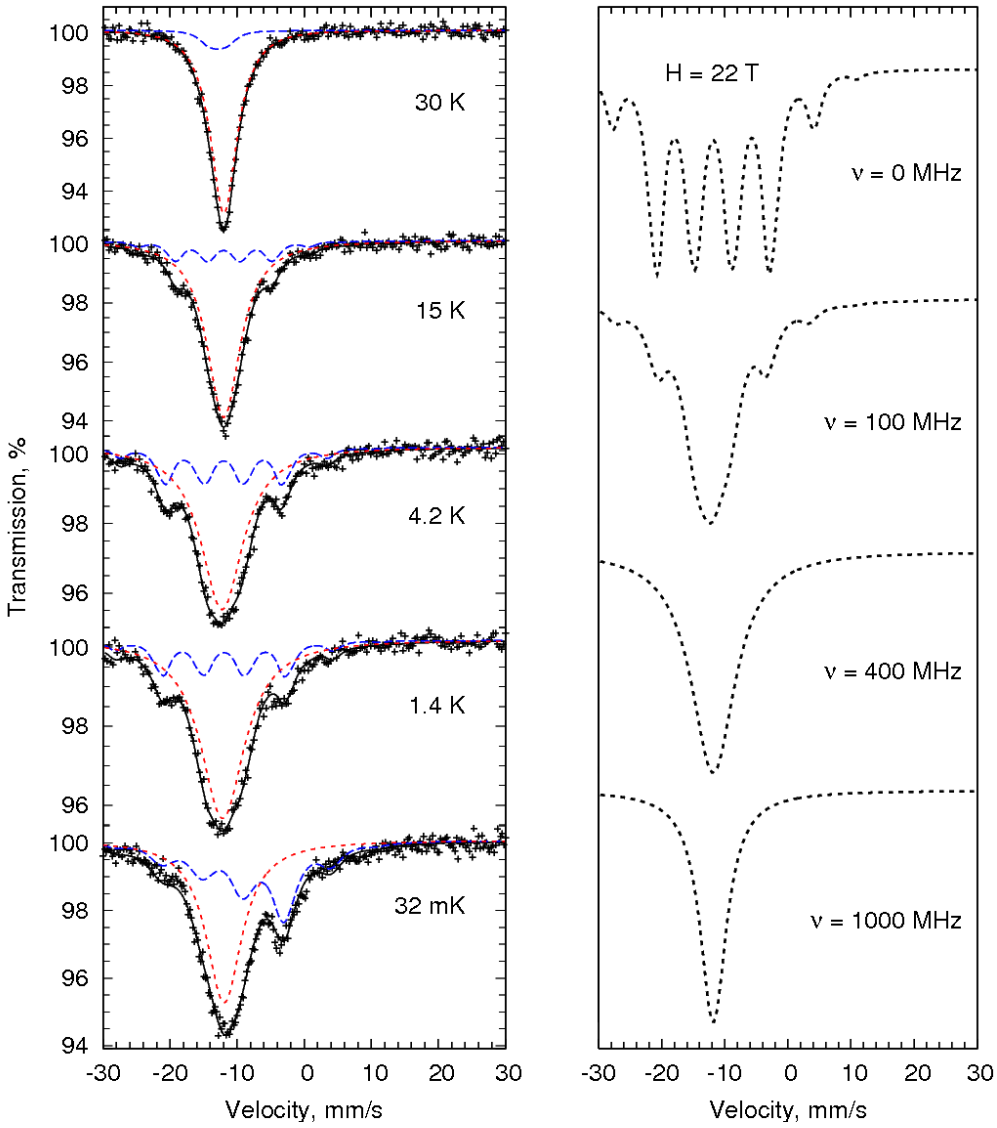
Larmor precession, ^{151}Eu



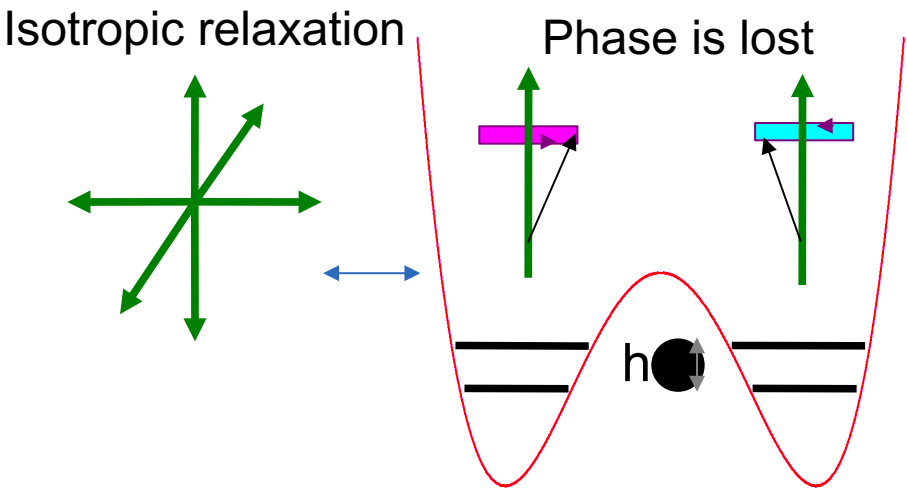


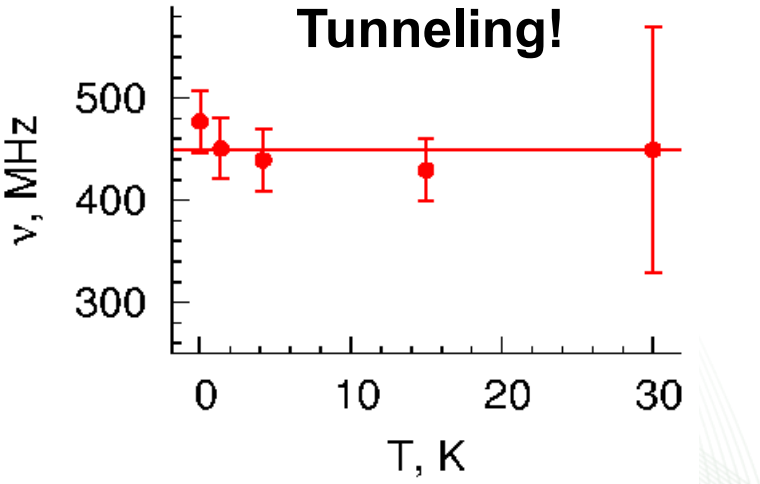


Relaxation spectra



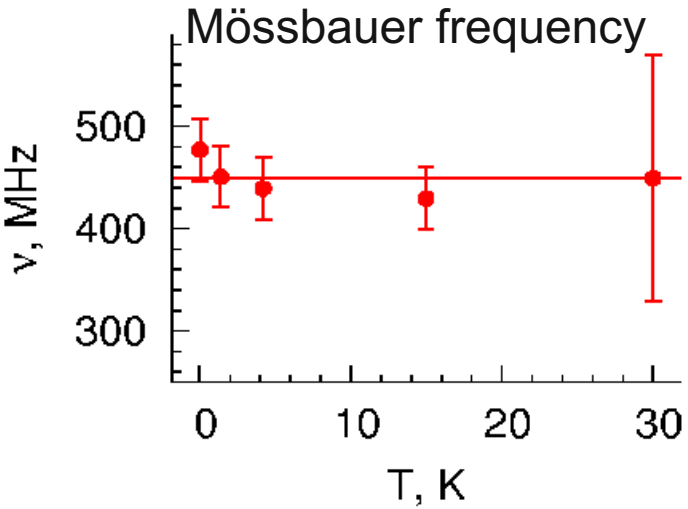
S. Dattagupta and M. Blume, Phys. Rev. B 10,4540 (1974).





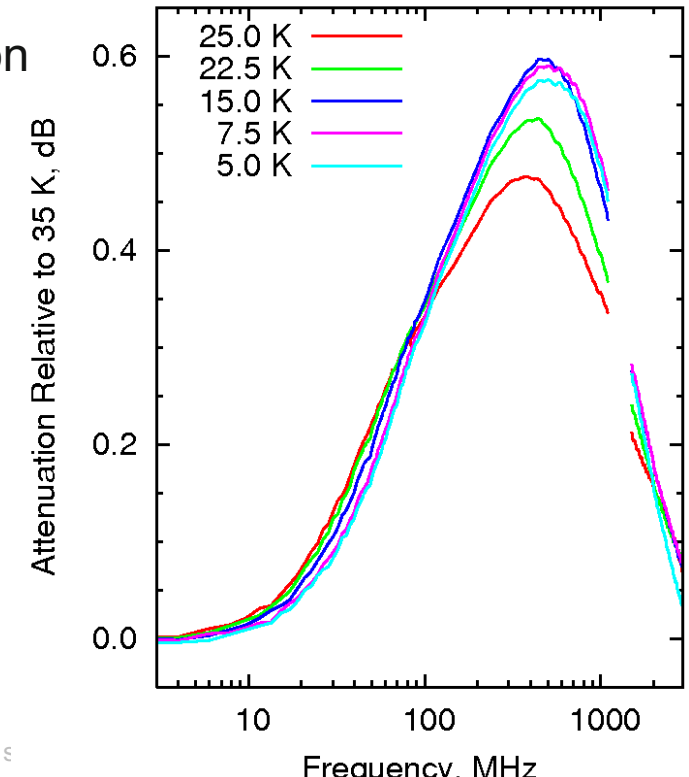
R. P. Hermann, V. Keppens, P. Bonville, G. S. Nolas, F. Grandjean, Gary J. Long, H. M. Christen, B. C. Chakoumakos, B. C. Sales, and D. Mandrus, *Phys. Rev. Lett.* **97**, 017401 (2006).

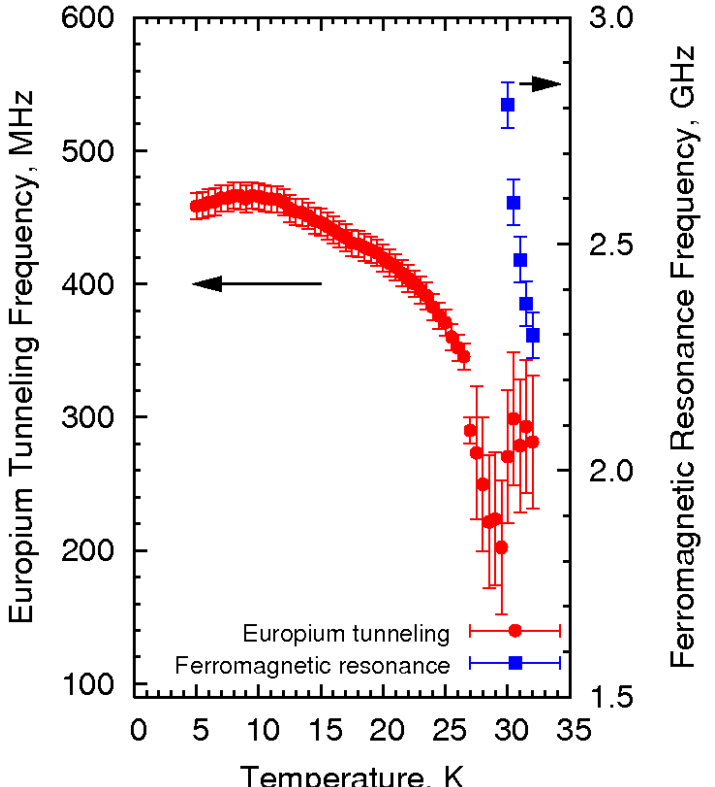
Tunneling dynamics



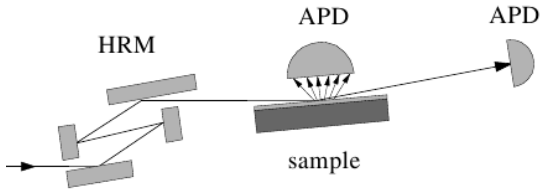
R. P. Hermann, V. Keppens, P. Bonville, G. S. Nolas, F. Grandjean, Gary J. Long, H. M. Christen, B. C. Chakoumakos, B. C. Sales, and D. Mandrus, *Phys. Rev. Lett.* **97**, 017401 (2006).

Microwave absorption

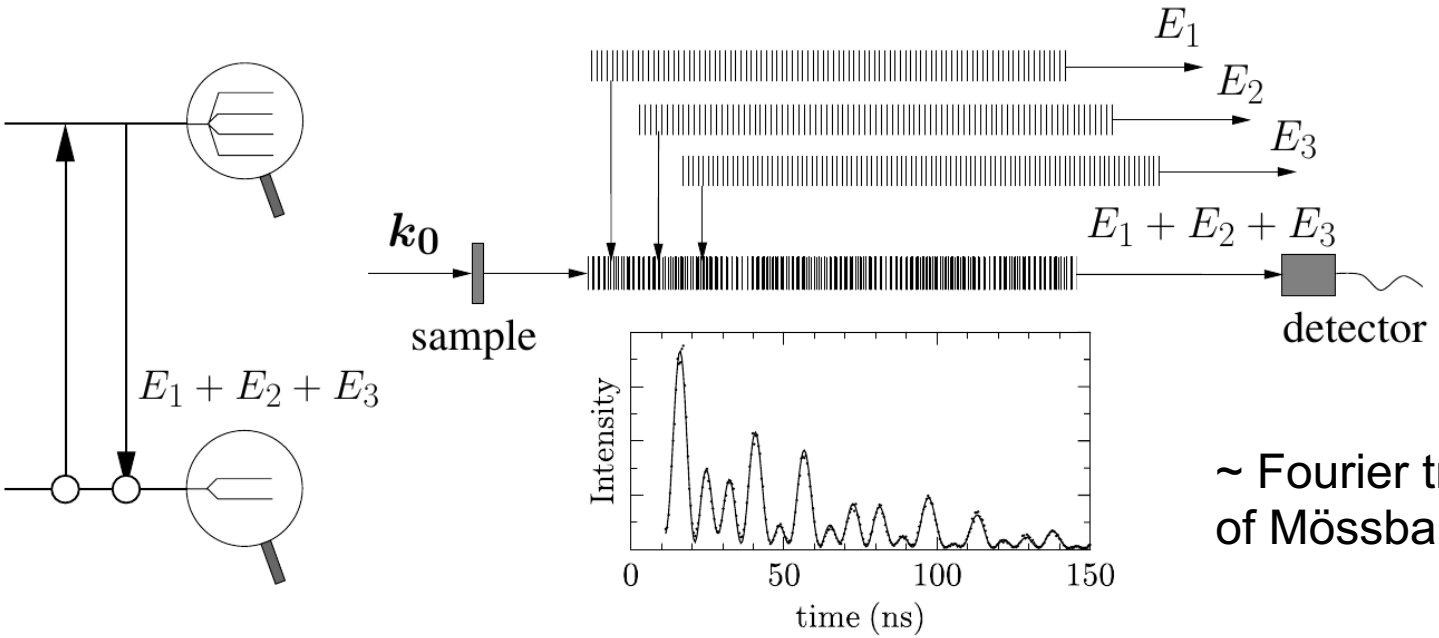




Nuclear forward scattering



Hyperfine splitting → Quantum beats



~ Fourier transform
of Mössbauer spectrum

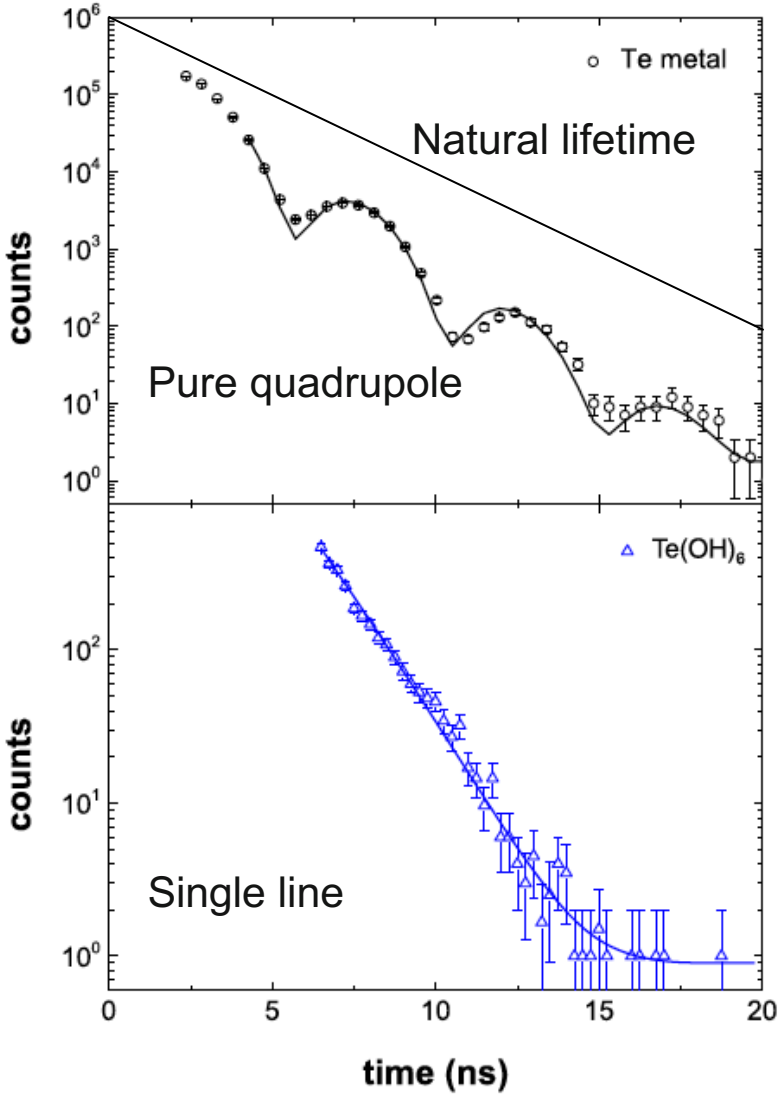
Multiple scattering →Dynamical beats

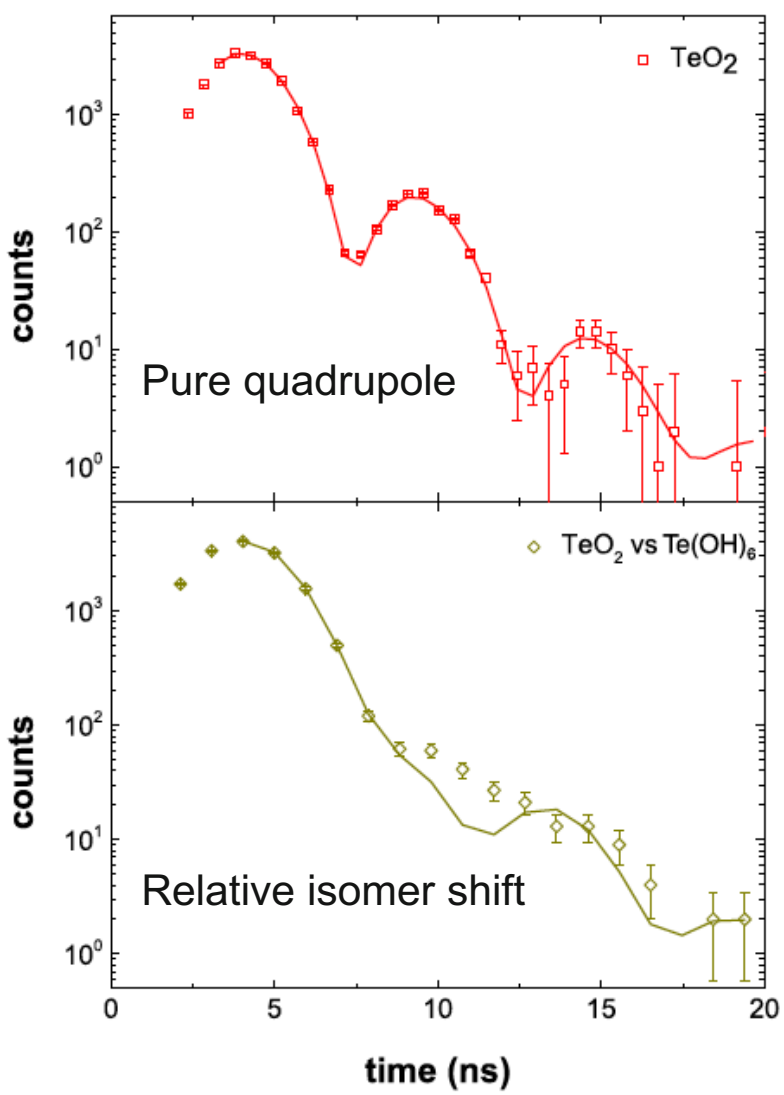
$$A(t) = \delta(t) - \gamma\, \mathrm{e}^{-t/2\tau_0}\, \frac{J_1(2\sqrt{\gamma t})}{\sqrt{\gamma t}} \quad \text{with} \quad \gamma = \frac{k_0 d\, f_0}{\tau_0}$$

… except for thickness
broadening

Röhlsberger R., Nuclear Condensed Matter Physics with Synchrotron Radiation, Springer Tracts in Modern Physics (2004)

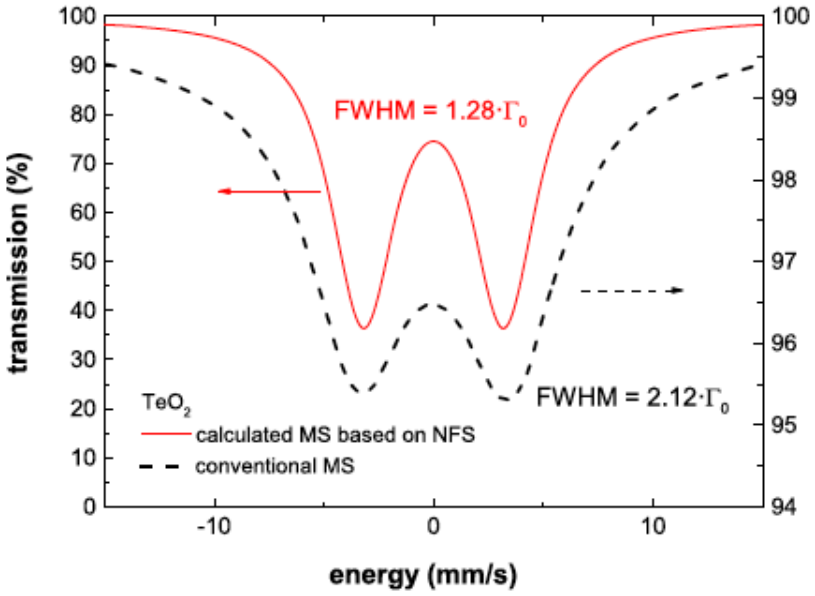
^{125}Te nuclear forward scattering

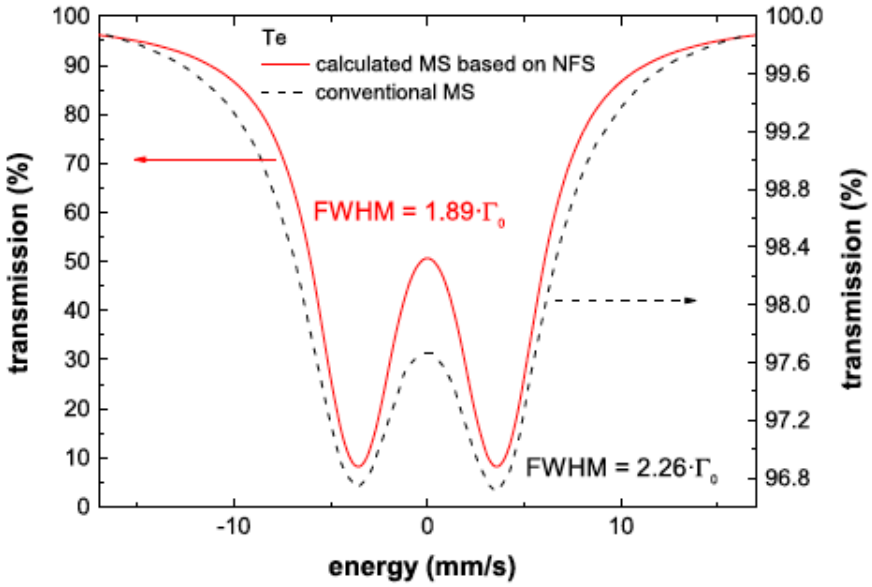




Klobes B. et al., *Hyperfine Interact* **226,** 713–719 (2014).

^{125}Te – NFS *vs.* Mössbauer spectroscopy





Intrinsic natural linewidth

Due to ^{125m}Te source broadening NFS is the more elegant solution for ^{125}Te Mössbauer spectroscopy

At ORNL:

Opportunity for ^{125}Te or ^{129}I MS by activating ^{124}Te or ^{128}Te in Mg_3TeO_6 or Ba_2MgTeO_6 at HFIR

Klobes B. et al., *Hyperfine Interact* **226,** 713–719 (2014).

New kids on the block

^{187}Os @ 9.78 keV
Bessas *et al.*, PRB (2015)

^{125}Te @ 35.4 keV
Wille *et al.*, Europhys Lett (2010)

^{121}Sb @ 37.1 keV
Wille *et al.*, Europhys Lett (2006)

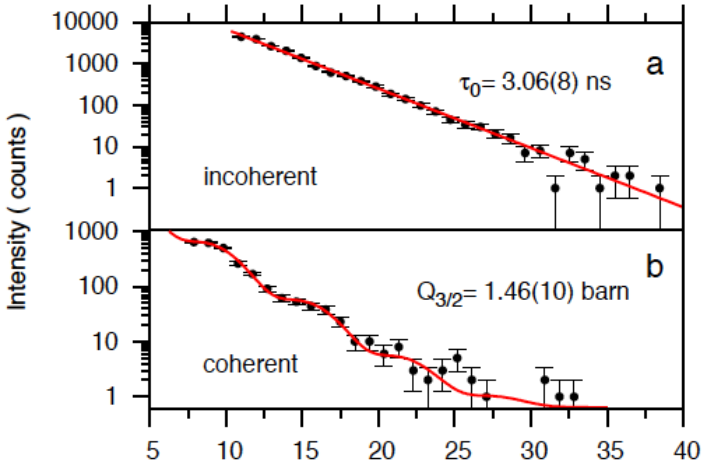
^{129}Xe @ 39.9 keV
Klobes *et al.*, Europhys Lett (2013)

^{61}Ni @ 67.4 keV
Sergueev *et al.*, PRL (2007)

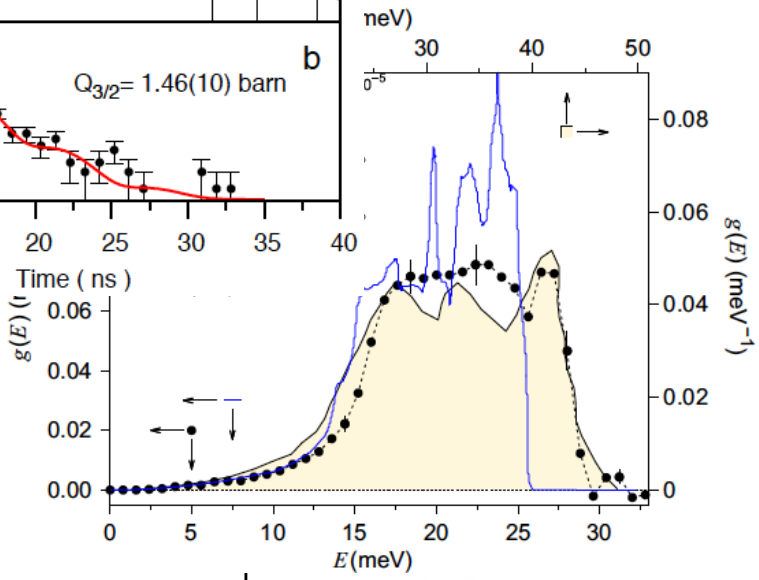
^{73}Ge @ 68.7 keV
Simon *et al.*, Europhys Lett (2013)

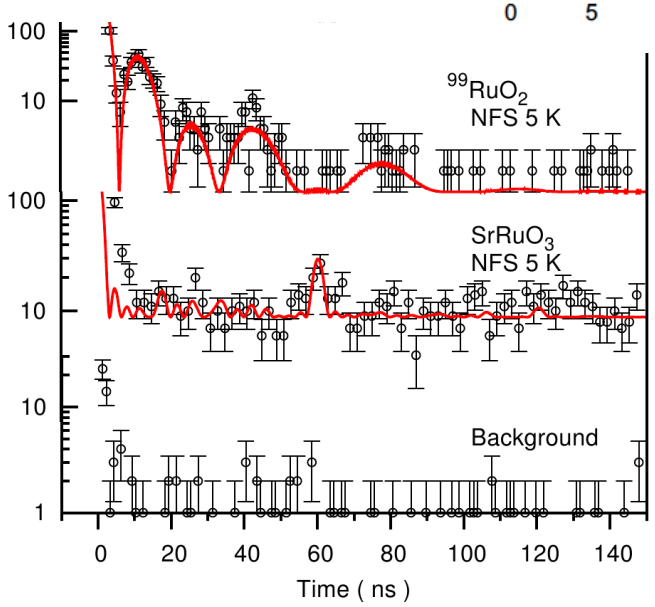
^{174}Yb @ 76.5 keV
Masuda et al., APL (2014)

^{99}Ru @ 89 keV
Bessas *et al.*, PRL (2014)



hcp Os, 295 K





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R. Rüffer and A. Chumakov, E.S.R.F.

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Helmholtz Association of Research Centers / The University of Tennessee / U. Liège .

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